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Division of Chemical Science

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(Otdelenie Khimicheskikh Nauk)

IN ENGLISH TRANSLATION

CONSULTANTS BUREAU, INC.

DENDRITIC CRYSTALLIZATION

by **D. D. SARATOVKIN**

2nd Edition,
Revised and Enlarged

Translated from Russian

THIS SIGNIFICANT volume has been extensively revised by the author from the 1953 edition; in particular with *fresh material derived from observations under the stereoscopic microscope.*

The first section deals briefly with some general concepts on crystallization, drawing an important distinction between *genetic* and *structural* types of crystals, including some aspects of the *defect crystal state.* The second section covers at length the illuminating ideas and observations of the 19th-century Russian metallurgist D. K. Chernov, who proposed many of the basic ideas of dendritic crystallization. The third section is an extended survey of current views on dendritic crystallization, in which the ideas of many Soviet and other scientists are briefly summarized and criticized. Section four presents the growth forms of real crystals; all types are reviewed, but only dendritic or closely related forms are selected for subsequent investigation.

Following sections discuss the causes and forms of crystal growth, with *detailed applications* to certain substances that have been extensively studied *(particularly the ammonium halides)*, and to eutectics in metal and organic systems; an extensively revised presentation on steel castings which provides a lucid explanation of how the various structures found in real castings can be fitted into the author's theory of dendritic crystallization. Nearly all the concepts developed earlier in the book are utilized in this final section.

The main bulk of the volume contains many *original* and *unpublished* ideas and observations, and is an excellent example of the modern macroscopic approach to the crystalline state by an experienced worker concerned with the infinite variety of real crystals—all of which is enhanced by a *profusion of explanatory line diagrams and sets of stereoscopic photographs.*

CB translations are by bilingual scientists, and include all photographic, diagrammatic and tabular material integral with the text.

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CORROSION OF SILICATE GLASSES BY ALKALINE SOLUTIONS

COMMUNICATION 3. INHIBITORS OF THE ALKALINE CORROSION OF GLASSES

V. S. Molchanov and N. E. Prikhid'ko

It is known that the breakdown of silicate glasses by neutral and, particularly, acid solutions is accompanied in the first moments of the process by a peculiar form of self-protection: the formation of a surface layer (or "film") consisting of breakdown products of the glass, mainly hydrated silica [1,2]. Depending on the nature of its porosity, this surface layer makes further interaction between the solution and the glass more or less difficult. On the other hand, alkaline solutions, which convert the silicon-oxygen structural units of silicates into a soluble form, do not allow a protective layer to form and in this case the breakdown of the glass is equivalent to its dissolution as a whole. Accordingly, in all experiments in which the surface area of the glass and the time during which it was exposed to the action of alkali were not great and the volume of solution was sufficiently large it was found that the rate of breakdown of the glass was constant and its extent directly proportional to the time. If, however, these conditions are not observed, so that large amounts of the breakdown products of the glass accumulate in the solution, an inhibition of corrosion, reminiscent of anodic passivity in metals [3], begins to develop.

Berger [4] was the first to describe a case of retardation of interaction between glass and an alkaline solution by products of this reaction. The "poisoning" of the breakdown of glasses in alkaline solutions was studied in greater detail by Geffcken [5], who found that such phenomena are caused not only by the breakdown products of the glass, but also, in a much greater degree, by addition of various compounds to the solution of alkali. Among these Geffcken drew attention particularly to aluminum hydroxide and potassium metasilicate, addition of which in amounts of only $10^{-3} - 10^{-4}$ g-equiv/liter reduced the rate of breakdown of the glass appreciably (as compared with the rate in pure caustic alkali solution). The smallness of the additions needed to affect the rate of breakdown made it possible to refer to such substances as inhibitors of the corrosion of the glass, in analogy with inhibitors of the corrosion of metals [6]. In later investigations by Wegst the exceptionally great inhibiting effect of beryllium compounds was established: by their addition to 0.25-2.5 N NaOH in an amount of 0.5% on the alkali content, the breakdown of the glass, according to Wegst [7], was reduced a hundredfold. Apart from beryllium, Wegst proposed the use of compounds of zinc, aluminum, antimony, tin, bismuth, barium, strontium, and also tannin, though the protective effects of the last six of these inhibitors were not characterized. It should be noted that somewhat earlier a detergent alkaline liquid containing some sodium aluminate was proposed by Cooper [8]. Molchanov and Ozeretskovskaia (see review article [2]), working with the very unstable glass TK10, confirmed the powerful inhibiting effect of beryllium, zinc, and aluminum compounds. Sasaki [9] and Furuuchi and Uno [10] also noted the inhibiting effect of aluminum and zinc compounds. Hence, the inhibiting action of compounds of these metals, and also of beryllium, can be regarded as proved by the results of several investigations. The views of Hurl and Wallington [11] on the high inhibiting effect of additions of sodium phosphate or silicate to sodium carbonate solution cannot be regarded as established.

In the course of the study of the corrosion of silicate glasses by alkaline solutions [12, 13] we obtained some results of interest for the understanding of the phenomenon of inhibition and for the more successful utilization of this phenomenon.

TABLE 1

Thickness (in microns) of Glass Layers Dissolved in the Presence of our Inhibitor (glass layers given in moles %)

No.	Type of glass	Name of glass or composition (mole %)	Without inhibitor	With inhibitor		
				BeO_4''	AlO_4'	ZnO_4''
1	—	Quartz, optical	0,8	0,1	0,1	0,3
2	Binary alkali-silicate	Na_2O 14,3	1,3	0,2	—	—
3		Na_2O 20,0	3,2	3,6	2,2	2,7
4		Na_2O 25,0	11	15,5	—	—
5		Na_2O 33,3	69	—	58	—
6		Li_2O 30	3,1	0,8	—	—
7		K_2O 20	336	530	650	—
8	Ternary	Na_2O 12·K_2O 8	17,3	13,8	11,7	—
9	Lead-containing	Optical FZ	2,2	0,7	0,4	—
10		Optical lead metasilicate·0.6 K_2O	25,3	3,1	2,8	1,4
11		Electrovacuum 3S4	2,5	0,4	0,5	—
12		Experimental, lead disilicate	3,4	0,4	—	—
13		" Na_2O 10·PbO 25·SiO_2 65	3,2	0,6	0,6	0,4
14		" Na_2O 13·PbO 32·SiO_2 55	7,2	0,4	1,5	—
15	Borosilicate	Optical K8	2,6	0,6	0,4	0,3
16		Laboratory Pyrex	7,3	0,6	1,0	0,4
17		Electrovacuum No. 46	7,6	0,4	1,0	0,7
18		" 3S11	7,6	1,4	1,4	—
19		" No. 17	14,9	2,4	1,9	—
20		" 3S8	17,3	6,2	1,3	—
21		" 3S9	27,0	7,6	4,8	—
22		Experimental Na_2O_7·B_2O_3 23·SiO_2 70	104,0	51,2	—	19,2
23	Barium-containing	Optical TK-10	7,1	2,3	1,7	0,8
24		Experimental.... Na_2O 12·BaO 23·SiO_2 65	4,4	—	—	0,4
25		Experimental Na_2O 13·BaO 32·SiO_2 55	4,8	0,3	0,9	—
26	Calcium-containing	Laboratory DG23	1,6	0,5	0,4	0,3
27		Experimental DG24	1,2	0,4	0,1	0,2
28		" DG29	1,3	0,2	0,3	0,2
29		Mirror	1,5	0,2	0,4	0,3
30		McInnes electrode glass	2,4	—	0,5	—
31		Experimental..... Na_2O 10·CaO 25·SiO_2 65	1,4	0,2	0,2	—
32		" Na_2O 13·CaO 32·SiO_2 55	1,6	0,22	0,7	—
33	Zirconium	Laboratory Ts-32	0,9	—	0,3	—
34	Boroantimony silicate	Optical 02	17,2	4,9	2,9	1,3
35	Beryllium	Experimental... Na_2O 10·BeO 25·SiO_2 65	1,5	0,35	0,30	—

TABLE 1 (Cont'd.

No.	Type of glass	Name of glass of composition (mole %)		Without inhibitor	With inhibitor		
					BeO_2^{2-}	AlO_2^-	ZnO_2^{2-}
36	Magnesium	Experimental	Na_2O 10·MgO 25·SiO_2 65	1,2	0,3	0,4	0,2
37		" "	Na_2O 13·MgO 32·SiO_2 55	1,8	0,4	0,1	—
38	Strontium	Experimental	Na_2O 10·SrO 25·SiO_2 65	4,1	—	—	0,4
39	Zinc-containing	Experimental	Na_2O 10·ZnO 25·SiO_2 65	2,6	0,3	0,5	0,3
40		" "	Na_2O 13·ZnO 32·SiO_2 55	3,4	0,6	0,8	—
41	Cadmium-containing	Experimental	Na_2O 10·CdO 25·SiO_2 65	1,1	0,4	0,6	—
42		" "	Na_2O 13·CdO 32·SiO_2 55	1,5	—	0,5	—

EXPERIMENTAL

We assessed the various inhibitors by comparison of the thicknesses of the layers of glass dissolved in presence and in absence of the protective substances in the solution used. The thickness dissolved was determined interferometrically: polished samples of glass were used, and the solution of alkali was allowed to act on a portion of the surface, while the remainder of the surface was protected by a sheet of rubber. Details of the experimental procedure and of the measurements are given in previous papers [12, 13]. We shall here confine ourselves to an indication of the main conditions: all the experiments were carried out in silver apparatus; the total area of glass surface in contact with the solution was 10 sq.cm, and the working surface was 0.5 sq. cm; the treatment solution was 0.5 N NaOH (950 ml), which was used at 90° and was stirred at 200 r.p.m; the duration of the action of alkali was four hours.

The first series of experiments was carried out on 42 glasses of the most varied types: quartz, double alkali, borosilicates, lead, barium, etc. As additives to the alkaline solution we used substances whose inhibiting effect was not in doubt: beryllium, aluminum, and zinc hydroxides. They were added as hydroxides in amounts calculated to give solutions of strength 0.016 N * with respect to beryllate, aluminate, and zincate ions. Table 1 gives the results of the experiments , and it can be seen that inhibition phenomena were to be observed in the case of the breakdown of 38 glasses out of the 42 studied; they were not observed for four glasses, all in the same group, i.e. simple sodium and potassium glasses that are very extensively attacked under our conditions. It is possible that at lower temperatures, at which the rate of dissolution is reduced, inhibition will be observed for these glasses also.

The fact that the breakdown of quartz glass, which does not contain any exchangeable cations, can be inhibited indicates that the inhibitors act not so much on the process of extraction of cations as on the breakdown of the silicon-oxygen part of the glass structure. In their effectiveness, the three inhibitor ions studied are almost the same, though one or the other of these ions may have the greater activity, depending on the composition of the glass. A maximum reduction of 18-fold in the corrosion can be effected by addition of the inhibitor. It is probable that the 100-fold reduction referred to by Wegst in his patents must be regarded as exaggerated. In the case of three glasses: quartz, TK10, and 02 (No. 1, 23, and 34 in Table 1), we determined the effect of various conditions on the action of the inhibitors.

Fig. 1 shows the relation of the effectiveness of inhibition to the alkali concentration (at two concentrations of inhibitor, 0.008 and 0.016 g-equiv/liter of BeO_2^{2-}). It is found that the inhibiting effect of the beryllate ion is preserved even in concentrated alkali solutions, though it is somewhat reduced. With increase in the

*A concentration of 0.016 N was selected because it is approximately equal to the limit of the solubility of beryllium hydroxide in 0.5 N NaOH.

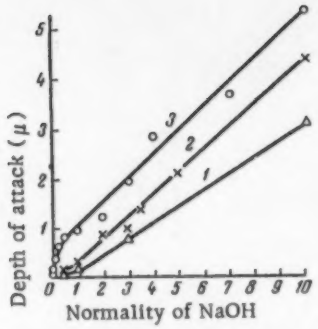

Fig. 1. Effect of BeO_2^{2-} ions on the breakdown of quartz glass in NaOh solutions: 1) with 0.016 g-equiv BeO_2^{2-} ; 2) with 0.008 g-equiv BeO_2^{2-}; without BeO_2^{2-} .

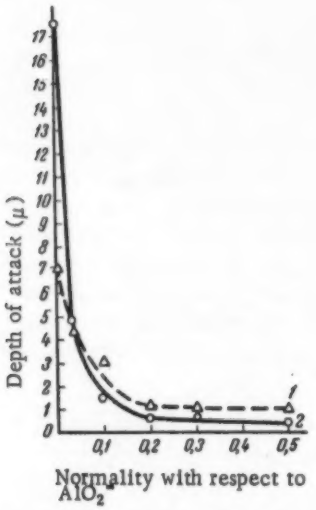

Fig. 2. Inhibition of the breakdown of glasses TK10 (1) and 02 (2) in 0.5 N NaOH with increasing amounts of AlO_2^- .

concentration of the inhibitor its effect increases. The relation of the effect of the inhibitor to its concentration is characterized more fully in Fig. 2 for the case of the corrosion of the glasses TK10 and 02 in presence of the aluminate ion. The effect of temperature on the inhibition effect is shown in Fig. 3. The action of the inhibitor is preserved over the whole of the temperature range studied, and its relative effect increases as the temperature rises. The beryllate ion acts as an inhibitor even in carbonate solutions.

Fig. 4, which characterizes the kinetics of the breakdown of the glass TK10 in sodium hydroxide solution, reveals an important detail of the action of inhibitors: constancy of the rate of the brakdown of glass in their presence. If the protective effect depended on a diffusion mechanism, i.e. if the inhibitor produced a protective film of appreciable thickness on the surface, the rate of breakdown would fall during the experiment and the thickness of the layer dissolved would change not in accordance with a straight line, but in accordance with a curved line. Such a case, for example, was observed by Kukolev and Simkhovich [14] in the alkaline breakdown of synthetic forsterite, the grains of which became enveloped in alkali-insoluble magnesium hydroxide with the result that the rate of breakdown diminished continuously.

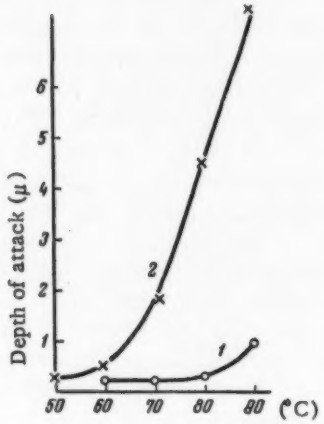

Fig. 3. Effect of temperature on the inhibiting effect of BeO_2^{2-} on the glass TK10 in 0.5 N NaOH: 1) with 0.016 g-equiv of BeO_2^{2-}; 2) without inhibitor.

The answer to whether or not the inhibiting effect is specific for beryllate, zincate, and aluminate ions, or whether it is shown by other ions, also, is given by Table 2, which contains results of measurements of the thicknesses of the layers dissolved for three glasses in 0.5 N NaOH containing 0.016 g-equiv/liter of the anion to be examined. The anions were introduced into the concentrated alkali in the form of the compounds indicated in the second column of Table 2. The resulting solutions were diluted with water until the above-indicated concentrations of alkali and inhibitor were attained. Table 2 shows that beryllate, zincate, and aluminate ions have the greatest effect and differ markedly from the other ions; we may therefore call them "strong inhibitors." The remaining anions retard corrosion to a much lesser extent, and some of them even accelerate corrosion. The effectiveness of the inhibitors depends on the composition of the glass. Thus, the breakdown of the glass TK10 is retarded by the stannate ion, but is considerably accelerated by vanadate, tetraborate, tungstate, chromate, phosphate, and chloride ions. The breakdown of the glass 02 is inhibited to some extent by all anions with the exception of

phosphate. The accelerating effect of anions can in many cases be correlated with the insolubility of their compounds with barium ions present in the glass. In spite of vigorous rotation of the glass samples in the solution, in some cases a compact incrustation of crystals formed; judging from Debye x-ray photographs, the crystals consisted of barium vanadate and chromate.

TABLE 2

Comparison of the Effects of Various Anions introduced into 0.5 N NaOH (duration of alkaline treatment 4 hours, temperature 90°)

Anion inhibitor	Form in which inhibitor added	Thickness of layer of glass dissolved (μ)		
		Quartz	TK10	02
Without inhibitor		0,8	7,1	17,2
Beryllate	Hydroxide	0,1	2,3	4,9
Aluminate	»	0,1	1,7	2,9
Zincate	Oxide	0,3	0,8	1,3
Tetraborate	Sodium salt	0,9	9,1	11,6
Silicate	» »	0,6	6,3	7,9
Chromate	» »	0,7	13,0	15,5
Phosphate	» »	0,7	12,5	31,3
Chloride	» »	0,7	10,5	8,0
Sulfate	» »	0,4	7,7	7,4
Molybdate	Ammonium salt	0,7	7,9	10,0
Tungstate	Trioxide	0,8	8,2	10,7
Vanadate	Pentoxide	0,5	12,6	14,6
Gallate	Metal	0,7	6,8	14,3
Stannate	Chloride	0,6	4,8	—

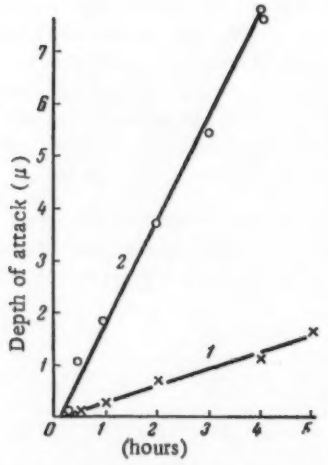

Fig. 4. Kinetics of the breakdown of the glass TK10 in 0.5 N NaOH: 1) with 0.016 g-equiv of BeO_2^{2-}; 2) without inhibitor.

EXPERIMENTAL RESULTS

Any explanation offered for the phenomenon of inhibition must take account of the following main facts: 1) In protecting glass from corrosion, inhibitor anions act "chemically," i.e. they affect the course of elementary processes of which the corrosion is made up; they do not form protective layers which would act as a mechanical barrier to the diffusion of the reagent to the unchanged glass; on introduction of the glass into the solution containing a given concentration of inhibitor a definite rate of dissolution of glass is established, and this rate is less than in absence of inhibitor and is constant. 2) Beryllate, zincate, and aluminate ions stand apart from other inhibitors, their power to protect glass being several times as great. 3) All silicate glasses are subject to inhibition.

A more or less detailed hypothesis on the mechanism of the inhibition of the corrosion of glasses was advanced some time ago by Berger and Geffcken [15]; they assumed that ion inhibitors, as a result of their high tendency to be sorbed on the silicon-oxygen groups of glass, occupy the active centers and so prevent hydroxyl ions from peptizing silicon-oxygen groups. In Berger and Geffcken's opinion, the extent to which the ions are sorbed is determined by

the law of Paneth, Fajans, and Hahn* concerning the preferential sorption of ions that give the least soluble compounds with ions contained in the sorbent.

Berger and Geffcken assumed that inhibition can be produced both by anions and by cations. We consider that Berger and Geffcken's hypothesis still retains its significance. The important characteristic of this phenomenon, namely that the rate of corrosion is not reduced to zero by the inhibitor, but is reduced considerably to a certain constant value, can be explained by the following considerations: ion inhibitors are sorbed on active centers of the glass surface, preferentially those characterized by the lowest activation energy for attack of the glass by hydroxyl ions. The reaction continues only at the less active centers associated with a higher activation energy, and this results in a general retardation of the corrosion process. In some respects Berger and Geffcken's scheme must be supplemented: 1) it must be considered that, though some cations, e.g. barium and calcium, are indeed capable of retarding the corrosion of silicate glasses, their inhibiting effect is considerably less than that of the strong inhibitors, which are anions; 2) Berger and Geffcken's view that there are glasses which are protected by some inhibitors and not by others is probably incorrect. Actually, the strong inhibitors, beryllate, zincate, and aluminate ions, have a fairly high retardation effect on the corrosion of all silicate glasses, with the exception of the group of simple water-soluble glasses, against the breakdown of which all inhibitors were ineffective under the conditions of our experiments. The reference of Berger and Geffcken to the law of Paneth, Fajans, and Hahn as a criterion of the inhibiting power of an ion requires some modification: it must be emphasized that for inhibition it is essential that the ion should have a high tendency to be sorbed and should form sparingly soluble compounds based on silicon-oxygen groups, the main structural element of silicate glasses, and not on cations. The three strong inhibitors conform exactly to this condition: their high tendency to be sorbed on silicon-oxygen groups is already to be expected because aluminum, beryllium, and zinc, e.g., in the aluminum silicates, are able to play a part analogous to that of silicon in the crystal chemistry of silicates and glasses. It is further known that in alkaline media stable sparingly-soluble compounds of the complex-silicate type can be formed. Thus, the formation of precipitates of sodium aluminum silicates when sodium silicate and aluminate solutions are mixed was proved in Lileev's investigations [16]. This synthesis was repeated by one of us and extended to sodium zinc and beryllium silicates. The existence of such compounds strongly supports the view that the strong-inhibitor anions are very strongly sorbed on the surface of silicate glasses.

In conclusion it is our pleasant duty to thank M. M. Dubinin and I. S. Lileev for advice and discussions.

SUMMARY

1. Some anions, in very low concentrations (about 0.01 g-equiv/liter), are able to effect a great reduction in the corrosion of glasses by alkaline solutions. Beryllate aluminate, and zincate ions are particularly effective, and it is proposed to refer to them as "strong inhibitors" of the alkaline corrosion of silicate glasses. These anions act as inhibitors of the alkaline corrosion of all silicate glasses except the very readily destroyed binary sodium and potassium glasses. The action of strong inhibitors is maintained in alkaline solutions over a wide range of concentrations and temperature, and also when sodium hydroxide solution is replaced by sodium carbonate solution. Other anions are much less effective than the strong inhibitors in retarding alkaline corrosion.

2. The experimental results are in accord with the views of Berger and Geffcken concerning the mechanism of the inhibition effect. This effect is due not to the formation of thick layers that render interaction between glass and solution mechanically difficult, but to the action of the inhibitor on the elementary processes of which the corrosion is made up.

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HYDROGEN EXCHANGE IN HETEROLYTIC REACTIONS. EXCHANGE OF HYDROGEN ATOMS IN THE REPLACEMENT OF IODINE IN ALKYL IODIDES

D. N. Kursanov, E. V. Bykova, and V. N. Setkina

As shown in numerous investigations, aliphatic carbonium ions can enter into hydrogen-exchange reactions with deuterium donors, e.g. deuterio acids [1-15]. On the basis of this it has been suggested that the hydrogen-exchange reaction can act as an indicator of the formation of carbonium ions in the intermediate stages of reactions and can therefore be applied in the study of reaction mechanisms. To determine whether this is so we investigated hydrogen exchange in heterolytic reactions whose mechanism is known from work with other methods of investigation.

The first examples that we studied [16, 17] gave encouraging results: reactions in which it has been shown by other methods that carbonium ions are formed intermediately were accompanied by hydrogen exchange. In the present paper we report results of an investigation of some nucleophilic replacements of iodine in alkyl iodides.

The mechanism of the replacement of halogen in alkyl halides was studied extensively by Ingold [18, 19], Hughes [18-22] Hinshelwood [23], and co-workers. It was shown that the mechanism of these reactions is determined principally by the structure of the alkyl attached to the halogen, and also by the polarity of the medium in which the reaction occurs. Tertiary alkyl halides show the highest tendency to undergo nucleophilic substitution by a unimolecular mechanism, i.e. with intermediate formation of carbonium ions, and primary alkyl halides show the highest tendency to undergo nucleophilic substitution by a bimolecular mechanism, i.e. without intermediate formation of carbonium ions. Increase in the polarity of the medium favors change of mechanism from bimolecular to unimolecular.

We investigated hydrogen exchange in alkyl groups in the nucleophilic replacement of iodine in alkyl iodides by hydroxyl:

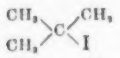
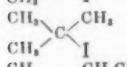
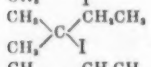
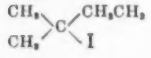
$$-\overset{|}{\underset{|}{C}}-I + H_2O \rightarrow -\overset{|}{\underset{|}{C}}-OH + I^- + H^+. \qquad (1)$$

We studied the direct hydrolysis of tertiary alkyl iodides with deuterium oxide. Under similar conditions (80% aqueous alcohol), according to the kinetic data of Hinshelwood [23], the hydrolysis of tertiary alkyl iodides proceeds by a unimolecular mechanism, i.e. with intermediate formation of carbonium ions. It would therefore be expected that, in the hydrolysis process, the tertiary alkyl iodides would undergo hydrogen exchange. Our results (Table 1) show that in the hydrolysis of alkyl iodides hydrogens of the alkyl group undergo exchange with deuterium: all the hydrogen atoms of tert-butyl iodide are replaced by deuterium, and the deuterium content of tert-pentyl iodide corresponds with exchange of all the α-hydrogen atoms. Hence, the data on hydrogen exchange in the hydrolysis of akyl iodides are in good agreement with kinetic data that indicate intermediate formation of carbonium ions.

The second reaction that we investigated was the exchange of iodine for another iodine atom in alkyl iodides:

$$-\overset{|}{\underset{|}{C}}-I_{(1)} + I^-_{(2)} \rightarrow -\overset{|}{\underset{|}{C}}-I_{(2)} + I^-_{(1)}. \qquad (2)$$

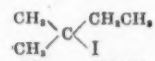
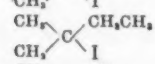
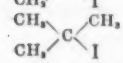
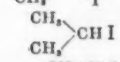
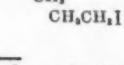
TABLE 1

Iodide	Molar ratio iodide / D_2O	Duration (hours)	Density excess of combustion water from alcohol			Exchange (% of that calculated for α-H)
			calculated*		found	
			for exchange of α-H)	for exchange of all H		
	1 : 5,3	14	52 950	52 950	33 000	62
	1 : 5,0	50,5	52 130	52 130	50 800	97,0
	1 : 5,5	85	42 200	50 200	40 380	96
	1 : 4,8	153	42 380	50 270	35 210	85

*Content of deuterium in alkyl group of alcohol.

This reaction has been studied in some detail by McKay, Neiman, and others [24-29]. These authors established that an exchange reaction occurs between iodine atoms of alkyl iodides and iodide ions of the reaction medium. We studied hydrogen exchange in the reaction of iodine exchange between alkyl iodides and 56% hydriodic acid. In view of the comparatively high polarity of the medium used in our experiments it would be expected that under our conditions there would be an increased tendency for the operation of the unimolecular mechanism, which proceeds through the intermediate formation of carbonium ions. When carbonium ions are formed we may expect that hydrogen exchange will occur as in the hydrolysis of tertiary alkyl iodides with water. Our results are presented in Table 2.

TABLE 2

Iodide	Density excess of original DI (γ/ml)	Duration of reaction (hours)	Density excess of combustion water from iodide (γ/ml)		Exchange (% of that calculated for α-H)
			calculated for exchange of α-H *	found experimentally	
	30 500	100	15 980	11 960	74,8
	30 500	214	16 350	14 500	88,7
	34 590	51	23 910	15 720	65,3
	34 590	51	22 960	76	0,3
	34 590	51	18 730	2	0

*In the calculation we assumed the coefficient of distribution between C − H and O − H bonds to be unity and that between C − H and I − H bonds to be 3.4 (from Varshavskii's calculations).

It will be seen from Table 2 that hydrogen exchange occurs in the case of tertiary alkyl iodides (tert-butyl and tert-pentyl iodides), but not in the case of a secondary alkyl iodide (isopropyl iodide) or of a primary alkyl iodide (ethyl iodide).

Hence, on the basis of the results on hydrogen exchange in the course of the replacement of iodine by another atom of iodine in alkyl iodides it may be considered that in the case of tertiary alkyl iodides this reaction proceeds through the intermediate formation of carbonium ions, but in the case of secondary and primary

alkyl iodides the reaction is not accompanied by intermediate formation of carbonium ions.

EXPERIMENTAL

Hydrolysis of Alkyl Iodides

tert-Butyl Iodide and Deuterium Oxide. A mixture of 6.16 g (0.033 mole) of tert-butyl iodide ($n^{20}D$ 1.4911; d^{20}_4 1.544) and 3.52 g (0.176 mole) of D_2O (density excess 99,000 γ/ml) was shaken at room temperature at 160 shakes/minute for 14 hours. The hydriodic acid liberated in the hydrolysis process was then neutralized with anhydrous potassium carbonate. The alcohol was separated and distilled over calcium hydride. To eliminate the hydrogen of the hydroxy group we converted the alcohol into its 3,5-dinitrobenzoic ester by treatment with 3,5-dinitrobenzoyl chloride [30]. After being crystallized from petroleum ether the ester melted at 140-141°. The deuterium content of the ester was determined by the usual method.

The density excess of the combustion water from the ester was 24,770 γ/ml; recalculated for C_4H_9 33,000 γ/ml; and calculated for the exchange of 9H in C_4H_9 52.950 γ/ml.

b) A mixture of 4.65 g (0.025 mole) of tert-butyl iodide and 2.53 g (0.126 mole) of D_2O (density excess 99,000 γ/ml) was shaken at room temperature at 160 shakes/minute for 50.5 hours. In other respects the experiment was carried out like the previous one. The tert-butyl 3,5-dinitrobenzoate, m.p. 138.5-140.5° (from petroleum ether), was subjected to combustion over cupric oxide.

The density excess of the combustion water from the ester was 38,080 γ/ml; recalculated for C_4H_9 50,800 γ/ml; and calculated for the exchange of 9H in C_4H_9 52,130 γ/ml.

tert-Pentyl Iodide and Deuterium Oxide. a) A mixture of 3.50 g (0.013 mole) of tert-pentyl iodide ($n^{20}D$ 1.4983; d^{20}_4 1.494) and 2.00 g (0.100 mole) of D_2O was shaken for 85 hours, and the DI liberated in the hydrolysis was then neutralized with anhydrous potassium carbonate; the alcohol was separated and distilled over calcium hydride. From the alcohol we prepared the p-nitrobenzoic ester, m.p. 83.5-85.0°. (from petroleum ether). The density excess of the combustion water from the ester was 29,610 γ/ml; recalculated for C_5H_{11} 40,380 γ/ml; and calculated for the exchange of 8H in C_5H_{11} 42,200 γ/ml.

b) A mixture of 3.46 g (0.012 mole) of tert-pentyl iodide and 1.73 g (0.084 mole) of D_2O (density excess 99,000 γ/ml) was shaken for 153 hours. Before neutralization the amount of DI present in the D_2O was determined and found to be 33%. The reaction products were then treated as in the previous experiment. The melting point of the p-nitrobenzoic ester was 84.2-84.7° (from petroleum ether).

The density excess of the combustion water from the ester was 25,820 γ/ml; recalculated for C_5H_{11}- 35,210 γ/ml; and calculated for the exchange of 8H in C_5H_{11}- 42, 380 γ/m).

Reaction of Alkyl Iodides with Hydriodic Acid

tert-Butyl Iodide and Hydriodic Acid. A mixture of 5.79 g (0.032 mole) of tert-butyl iodide ($n^{20}D$ 1.4910; d^{20}_4 1.543) and 10.79 g of 56% DI (sp.gr. 1.912) (density excess 34,590 γ/ml) was shaken mechanically for 51 hours. The tert-butyl iodide isolated after the reaction was shaken with mercury to remove traces of iodide and distilled. The constants of the iodide after the experiment were $n^{20}D$ 1.4980; d^{20}_4 1.557.

The density excess of the combustion water from the iodide after the experiment was 15,720 γ/ml; calculated for the exchange of 9H in C_4H_9 23,910 γ/ml.

tert-Pentyl Iodide and 56% Hydriodic Acid. a) A mixture of 4.03 g (0.020 mole) of tert-pentyl iodide ($n^{20}D$ 1.4983, d^{20}_4 1.494) and 7.10 g of 56% DI (density excess 30 500 γ/ml) was shaken mechanically for 100 hours. The constants of the tert-pentyl iodide after the experiment were $n^{20}D$ 1.4980; d^{20}_4 1.511.

The density excess of the combustion water from the iodide was 11,960 γ/ml; calculated for the exchange of 8H in C_5H_{11} 15,980 γ/ml.

b) A mixture of 3.18 g (0.016 mole) of tert-pentyl iodide and 5.97 g of DI (density excess 30.500 γ/ml) was shaken mechanically for 153 hours. The constants of the iodide after the experiment were $n^{20}D$ 1.4978; d^{20}_4 1.514.

The density excess of the combustion water from the iodide was 14,500 γ/ml; calculated for the exchange of 8H in C_5H_{11} 16,350 γ/ml.

Isopropyl Iodide and Hydriodic Acid. A mixture of 3.46 g (0.020 mole) of isopropyl iodide ($n^{20}D$ 1.4980; d^{20}_4 1.700) and 6.05 g of 56% DI (density excess 34,590 γ/ml) was shaken mechanically for 51 hours. The further procedure was as in the previous experiment. The constants of the isopropyl iodide after the experiment were $n^{20}D$ 1.4980; d^{20}_4 1.703.

The density excess of the combustion water from the isopropyl iodide was 76 γ/ml; calculated for the exchange of 6H in C_3H_7 22,960 γ/ml.

Ethyl Iodide and Hydriodic Acid. A mixture of 3.58 g (0.023 mole) of ethyl iodide (n^{20}_4 1.5124; d^{20}_4 1.9357) and 7.80 g of 56% DI (density excess 34.590 γ/ml) was shaken mechanically for 51 hours. The constants of the ethyl iodide after the experiment were $n^{20}D$ 1.5124; d^{20}_4 1.9356.

The density excess of the combustion water was 2γ/ml; calculated for the exchange of 3H in C_3H_7 18.730 γ/ml.

SUMMARY

1. The possibility of applying the hydrogen-exchange reaction in the study of the mechanism of heterolytic reactions was investigated. A study was made of hydrogen exchange a) in the hydrolysis of tertiary alkyl iodides (tert-C_4H_9I and tert-$C_5H_{11}I$) with water enriched with deuterium oxide, and b) during the exchange of iodine for another iodine atom in alkyl iodides (C_2H_5I, i-C_3H_7I, tert-C_4H_9I, and tert-$C_5H_{11}I$) in reaction with 56% HI enriched with deuterium iodide.

2. It was shown that hydrogen exchange in C – H bonds is observed in those reactions which, according to kinetic investigations, proceed by a unimolecular mechanism, i.e. with intermediate formation of carbonium ions. It was shown, in particular, that the hydrolysis of tertiary alkyl iodides (C_4H_9I and $C_5H_{11}I$) and replacement of iodine by iodine in tertiary alkyl iodides, which proceed by an SN_1 mechanism, are accompanied by hydrogen exchange reactions of secondary and primary alkyl iodides, which permits us to assume a bimolecular mechanism for these reactions.

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PROPERTIES AND STRUCTURE OF NiO – Al_2O_3 CATALYSTS
COMMUNICATION 1. EFFECT OF COMPOSITION AND CONDITIONS OF THERMAL TREATMENT ON ACTIVITY AND SELECTIVITY

A. M. Rubinshtein, A. A. Slinkin, and N. A. Pribytkova

During the last decade several large investigations have been published on the physical structure of NiO – – Al_2O_3 catalysts. Thus, a detailed description has been given [1] of the phase composition and structure of co-precipitated gels of nickel and aluminum hydroxides dried in the air and roasted at 500°, 700°, and 1000°. In another investigation [2] a magnetochemical study was made of NiO – Al_2O_3 catalysts prepared by impregnation, their activities being determined for the hydrogenation of benzene after reduction of the nickel to the metal, and in a recently published investigation [3] analogous coprecipitated catalysts were subjected to magnetochemical investigation. In none of these investigations, each of which has provided many interesting and valuable data, were the measurements accompanied by the determination of the catalytic activity of the NiO – Al_2O_3 in any reaction. In the investigation [2] this was done only after reduction of the nickel.

Nevertheless, the binary system NiO – Al_2O_3 is of considerable interest from the point of view of catalysis, because each of its components can be used directly as a catalyst: NiO in dehydrogenation reactions, and Al_2O_3 in dehydration reactions. A mixture of these catalysts is of interest from the point of view of the study of selectivity, e.g. in the decomposition of alcohols, in which both these reactions are possible. Moreover, NiO – Al_2O_3 mixture is an intermediary in the preparation of Zelinskii nickel catalyst [4], which is used in hydrogenation and dehydrogenation processes and has been studied by x-ray analysis [5]. Investigation of the effect of thermal treatment on such catalysts can give valuable information on the conditions of topochemical reactions, e.g. the formation of the spinel $NiAl_2O_4$, which are possible in such a system, which is a special case of binary systems consisting of mono- and sesqui-oxides, which are frequently used in catalysis.

In view of the fact that the above-mentioned investigations were not directly associated with catalysis and important structural characteristics, e.g. porous structure, were not examined, we decided to make a detailed study of the relation of structure and catalytic properties to composition and conditions of thermal treatment for the case of NiO – Al_2O_3 catalysts, their activity and selectivity being estimated for the decomposition of isopropyl alcohol, which is known to be uncomplicated by side or consecutive reactions at moderate temperatures. Determinations of structure were carried out by adsorption, x-ray, and magnetic methods, and in particular cases also by electron diffraction and electron microscopy. The results of the structural investigations form the subject of future communications, because the extensive material obtained in this investigation cannot be presented within the limits of a single paper.

EXPERIMENTAL

1. We prepared the NiO – Al_2O_3 catalysts from mixtures of 10% solutions of nickel and aluminum nitrates, which were precipitated as hydroxides by 10% ammonia solution at room temperature with vigorous stirring until pH 8 was attained (the pH was measured with an LP-5 potentiometer). The mixtures of hydroxides were washed 5-6 times by decantation and filtered, and the moist paste was extruded through dies and air-dried at 110°. Separate portions of each of the mixtures of hydroxides of the various compositions were roasted for seven hours in the air at 400°, 600°, and 750° (in some cases also at 900°), cooled in a desiccator, and kept under conditions precluding access of moisture. The diameters of the dried roasted grains of catalysts of various compositions

varied in the range 1.1-1.3 mm. The catalysts varied in color, depending on the NiO content and roasting temperature, from light to dark green and even to bright blue.

The amounts of material taken were calculated so as to give mixtures of hydroxides containing 5, 10, 15, 25, 50, 75, 100, and 150 moles of NiO for each 100 moles of Al_2O_3, but analysis of the catalysts for nickel content showed that the actual amounts of NiO were 4.2, 10.3, 15.8, 24.5, 46, 105, and 145 moles per 100 moles of Al_2O_3. As the amounts of the components taken were determined fairly accurately, the discrepancies between the calculated and actual compositions of the catalysts can be explained by the formation of some soluble ammonia complex of nickel in the precipitation, with removal of the components to differing extents during washing of the precipitates of hydroxides.

TABLE 1

Compositions, Bulk Densities (d), and Specific Surfaces (S in sq.m/g)of $NiO - Al_2O_3$ Catalysts

NiO taken (moles % on Al_2O_3)	Composition of catalyst according to analysis (moles %)		Roasting temperature (°C)						
			400		600		750		900
	Al_2O_3	NiO	d	S	d	S	d	S	S
0	100	0	0,82	284	—	—	0,90	135	—
5	96	4	0,90	284	0,87	190	0,90	156	—
10	90,9	9,1	0,90	310	0,87	198	0,90	156	—
15	86,3	13,7	0,80	331	0,77	206	0,86	104	—
25	80,3	19,7	0,76	282	0,77	210	0,76	136	—
50	68,5	31,5	0,76	265	0,80	192	0,86	153	72
75	59,5	40,5	0,73	225	0,83	187	0,90	129	—
100	48,5	51,5	0,90	229	0,90	184	0,96	145	57
150	41,0	59,0	0,93	221	0,90	165	0,90	123	66
	0	100	0,66	16	—	—	—	—	—
5	Repeat preparations		0,86	360	0,83	250	0,83	140	—
10			0,90	345	0,9	220	0,90	172	—
15			0,80	365	0,83	230	0,83	178	—
50			—	220	0,90	174	—	—	—

Table 1 gives the molar compositions of the catalysts, their bulk densities, and their specific surfaces. In the determination of bulk density, catalyst was placed in a measuring cylinder and consolidated by shaking until there was no further change in volume; 3 cc of it was then weighed accurately within 0.01 g. Specific surfaces were determined by adsorption of benzene vapor at 20° under flow conditions according to the procedure described in [6]. New samples were prepared of some of the catalysts, the conditions being fairly close to those used previously: data characterizing these preparations and also the reproducibility of the catalysts investigated are included in Table 1.

2. Determination of the activities of the catalysts in the decomposition of isopropyl alcohol was carried out with absolute i-C_3H_7OH($n^{20}D$ 1.3775) obtained by drying the azeotropic mixture containing 12.5% of water with calcium and distilling the product over a little sodium to remove traces of water. Activities and selectivities were determined over the temperature range 230-290° for the reactions

$$CH_3CHOHCH_3 \begin{cases} \rightarrow CH_3CH = CH_2 + H_2O \\ \rightarrow CH_3COCH_3 + H_2 \end{cases}$$

In the experiments at 230° and 245° only the most active catalysts were used. The experiments were carried out in the flow apparatus described previously [7]; the temperature of the electric block furnace was controlled within about 0.5° by means of an electronic regulator. The regular feed of the alcohol to the reactor was effected by an injector system. In all experiments the volume of catalyst was 3 cc and the space velocity of the feed of alcohol was 1-hour $^{-1}$.* Before the measurements were begun, the gas in the apparatus was displaced by products

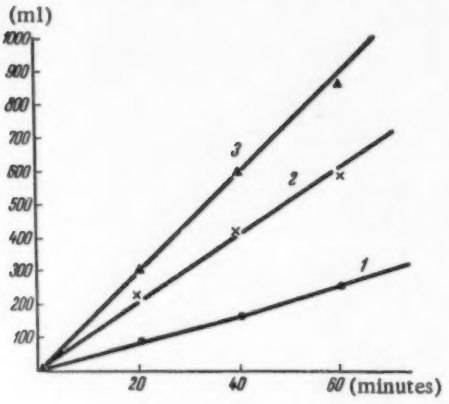
*As in original – Publisher's note.

TABLE 2

Volumes of C_3H_6 and H_2 (at STP) Liberated from 1 ml of Isopropyl Alcohol Passed at a Space Velocity of 1 $hour^{-1}$, and the Total Conversion (%) in One Passage (in parentheses)

Catalysts roasted at 400°						Catalysts roasted at 600°					Catalysts roasted at 750°					Catalysts roasted at 900°		
Temperature of experiment	230	245	260	275	290	230	245	260	275	290	230	245	260	275	290	260	275	290
Addition of NiO (moles % on Al_2O_3)	C_3H_6/H_2	C_3H_6/H_2	C_3H_6/H_2	C_3H_6/H_2	C_3H_6/H_2	C_3H_6/H_2	C_3H_6/H_2	C_3H_6/H_2	C_3H_6/H_2	C_3H_6/H_2	C_3H_6/H_2	C_3H_6/H_2	C_3H_6/H_2	C_3H_6/H_2	C_3H_6/H_2	C_3H_6/H_2	C_3H_6/H_2	C_3H_6/H_2
0	—	96,5 (33,0)	228,0 (78,8)	289,4 (99,0)	—	—	—	—	—	—	104,7 (35,8)	144,0 (49,2)	258,0 (87,3)	285,5 (97,8)	—	—	—	—
5	51,3 (17,0)	115,2 (40,0)	212,4 (73,0)	—	—	74,3 (25,5)	138,6 (37,5)	250,7 (85,8)	—	—	83,3 (28,4)	172,3 (58,7)	250,4 (85,8)	—	—	—	—	—
10	61,8 (21,0)	132,6 (46,0)	206,7 (70,0)	294,9 (100,0)	—	161,4 (55,0)	247,8 (85,0)	—	—	—	135,9 (46,3)	234,0 (79,8)	—	—	—	—	—	—
15	—	107, (36,5)	196,8 (67,5)	268,5 (92,0)	—	150,3 (51,5)	252,6 86,5	—	—	—	89,4 (30,4)	184,5 (63,0)	262,1 (89,4)	—	—	—	—	—
25	—	71,7 (2 ,5)	173,1 (59,0)	252,6 (86,0)	—	87,6 (30,0)	129,6 (44,5)	245,0 (83,8)	—	—	72,6 (24,8)	165,6 (56,6)	274,0 (93,4)	—	—	—	—	—
50	—	50,4 (17,2)	102,6 (35,5)	199,7 (68,0)	258,6 (88,0)	—	98,2 (33,5)	172,2 (58,0)	274,1 (94,0)	—	—	160,8 (54,7)	269,1 (91,0)	—	—	73,0 (25,0)	80,0 (27,4)	—
75	—	—	67,2 (26,0) /9,0	174,0 (66,5) /19,5	222,0 (79,4) /10,2	—	75,0 (27,3) /4,8	157,2 (55,3) /4,8	253,8 (89,0) /6,3	—	—	90,3 (33,6) /8,1	204 (72,5) /8,4	275,4 (9 ,0) /8,7	—	—	—	—
100	—	—	30,9 (29,0) /53,5	109,8 (58,0) /62,1	195,6 (87,0) /60,0	—	—	75,0 (35,0) /26,7	174,0 (71,8) /35,7	240 (94,0) /30,3	—	—	42,3 (24,7) /33,0	104,7 (51,5) /46,2	193,6 (86,4) /58,8	20,4 (19,0) /37,2	42,0 (35,8) /63,0	92,7 (61,3) /87,0
150	—	—	40,2 (36,5) /6 1,5	121,6 (61,0) 58,0	190,8 (87,0) /66,0	—	—	48,6 (25,8) /25,2	120,0 (53,5) /36,0	231 (91,0) /34,5	—	—	46,2 (29,6) /40,5	122,1 (59,3) /51,9	189,0 (83,7) /57,0	—	15,0 (20,4) /42,9	54,0 (48,3) /91,5

of the decomposition of isopropyl alcohol at the temperature of the experiment. Reaction rates were estimated from the volumes (reduced to STP) of propene and hydrogen liberated. The gaseous reaction products were analyzed in a GIAP apparatus: apart from the components indicated, the gas mixture contained a very small amount of carbon dioxide (0.1-0.2%). Liberation of gas during the experiments proceeded in a uniform fashion, as can be seen from the graphs obtained at different temperatures (1, 245°; 2, 260°; 3, 275°) with a catalyst containing 80.3 moles % of Al_2O_3 and 19.7 moles % of NiO roasted at 400° (see figure). Table 2 gives the experimental results obtained with the main series of catalysts. It must be emphasized that dehydrogenation (H_2) occurred only with catalysts in which the addition of NiO was 75 moles % (on Al_2O_3) or more.



The catalyst samples obtained in the repeat preparations had activities that agreed satisfactorily with those of the catalysts in the main series. Thus, the catalyst with an addition of 5% of NiO roasted at 400° gave 58.7 ml of C_3H_6 at 230°, 105 ml at 245°, and 228.1 ml at 260°; when roasted at 750° it gave 90 ml at 230° and 279 ml at 260°. The catalyst with an addition of 15% of NiO roasted at 600° gave 140 ml of C_3H_6 at 230° and 282 ml at 245°. Over the catalyst with a 50% addition (400°), 97.9 ml of C_3H_6 was liberated at 245° and 142 ml at 260°. In some cases the discrepancies between these results and those of the main series were somewhat greater and reached 10%, which, however, may be regarded as acceptable.

EXPERIMENTAL RESULTS

Table 1 shows that rise in the temperature at which the catalysts are roasted has little effect on the bulk density, but results in a considerable change in the specific surface. The highest specific surface S is possessed by catalysts with an addition of 5-15 moles per cent of NiO; for these the specific surface is greater than that of Al_2O_3 prepared under the same conditions; with further increase in the NiO content the specific surface falls to values below that of Al_2O_3. With rise in the temperature of roasting the relation between S and catalyst composition becomes obscure: as we pass from 400° to 750° S falls by about 50%, except in the case of the catalyst with a 15% addition of NiO, for which S is reduced by about 70%. There is a still sharper fall in S in the range 750-900°, in which it again falls by about 50%. The values of S are applied in the evaluation of the specific activity A_{sp}, which we have expressed (Table 3) as the number of $i\text{-}C_3H_7OH$ molecules reacting in the given way (dehydrogenation or hydration) at 1 sq. m of surface in 1 second; in Table 3 we give values of $A_{sp} \cdot 10^{-12}$.

Examination of the effect of thermal treatment on the A_{sp} values of the catalysts leads to the conclusion that in the range 400-750°, in which the phase transition $\gamma\text{-}Al_2O_3 \longrightarrow \alpha\text{-}Al_2O_3$ cannot yet occur, rise in temperature of roasting results in increase in the value of A_{sp} for the dehydration reaction, as can be seen from the way in which A_{sp} for dehydration changes at all experimental temperatures. As regards the dehydrogenation reaction, which occurs only on catalysts with the highest addition of NiO, here again catalysts roasted at 750° are more active than those roasted at 400°, though there are considerable discrepancies in the data for samples roasted at 600°.

Since, in the case of dehydration, the observed effect of thermal treatment on A_{sp} is preserved even for Al_2O_3 itself without additions, it can be maintained that A_{sp} increases as a result of progressively increasing dehydration of the catalyst with rise in temperature. There are indications in the literature that Al_2O_3 with optimum adsorption and dehydrogenation properties* is obtained by roasting it at about 400° [8], but these data refer to unit weight of Al_2O_3 and not to A_{sp}. The lowering of total activity with rise in temperature of roasting is apparently due to a great reduction in surface which is not compensated for by the change in A_{sp}. Moreover, rise in A_{sp} with temperature of roasting in the range indicated can be associated also with phase transitions. The polymorphism of Al_2O_3 is fairly complex [9, 10], and what is known in catalysis by the collective name of $\gamma\text{-}Al_2O_3$ refers actually to several phases (η, k, ϵ, θ and γ) formed under various conditions. There are

*Here "dehydrogenation" should probably read "dehydration."

unfortunately no data concerning the catalytic activities of these modifications of Al_2O_3; we propose to determine these in the near future.

TABLE 3

Specific Activities of Catalysts for the Dehydration (C_3H_6) and Dehydrogenation (H_2) of Isopropyl Alcohol, Expressed as Number of Molecules Reacting at 1 sq. m of Surface in 1 second (in the table we give values of $A_{sp} \cdot 10^{-12}$)

NiO added to catalyst (moles % on Al_2O_3)	Temperature of roasting of catalyst	Temperature of experiment (° C)									
		230		245		260		275		290	
		Reaction									
		C_3H_6	H_2	C_3H_6	H_2	C_3H_6	H_2	C_3H_6	H_2	C_3H_6	H_2
0 (pure Al_2O_3)	400	—	—	1,26	0	2,97	0	3,69	0	—	—
	750	2,61	0	3,6	0	6,39	0	7,20	0	—	—
5	400	0,72	0	1,62	0	3,06	0	—	—	—	—
	600	1,53		2,79		5,22					
	750	2,07		4,50		6,30					
10	400	0,63	0	1,44	0	2,25	0	3,15	0	—	—
	600	3,06		4,77		—	—	—	—	—	—
	750	3,78		6,47		—	—	—	—	—	—
15	400	—	0	1,26	0	2,34	0	3,33	0	—	
	600	3,60		6,03		—	—	—	—	—	—
	750	3,15		6,66		9,36	0	—	—	—	—
25	400	—	0	1,17	0	2,70	0	3,96	0		
	600	1,89		2,79		5,22		—	—	—	—
	750	2,16		4,86		8,10		—	—		
50	400	—	—	0,81	0	1,62	0	3,15	0	4,14	0
	600	—	—	2,25		3,87		6,30		—	—
	750	—	—	4,14		7,20		—		—	—
75	400	—	—	—	—	1,26	0,18	3,42	0,36	,32	0,18
	600	—	—	—	—	1,80	0,09	3,78	0,09	6,03	0,18
	750	—		2,70	0,27	6,12	0,27	8,28	0,27	—	—
100	400	—	—	—	—	0,45	0,81	1,62	0,90	2,88	0,90
	600	—		—	—	1,53	0,54	3,69	0,72	5,04	0,63
	750	—		1,35	0,81	2,52	1,08	4,59	1,44	—	—
150	400	—	—	—	—	0,72	1,08	2,16	1,08	3,33	1,17
	600	—	—	—	—	1,08	0,54	2,70	0,81	5,22	0,81
	750	—		—	—	1,35	1,17	3,69	1,53	5,67	1,71

A comparison of values of A_{sp} for catalysts of different compositions shows that in experiments at 245° and higher, catalysts having additions of up to 70 moles per cent of NiO are more active than Al_2O_3 and further increase in NiO content lowers the dehydrating activity and leads to dehydrogenation of part of the alcohol. From Table 3 it follows further that A_{sp} varies nonlinearly with NiO content; depending on the roasting temperature, the point of maximum activity varies in the range 5-15 moles per cent of NiO. This is a typical optimum with respect to composition, since A_{sp} is referred to unit surface area; it can be explained by change in the lattice constant of Al_2O_3 as a result of the solution of NiO in it (geometric factor) and by change in the electronic state of the catalyst as a result of the differing distribution of NiO at different concentrations. These matters are examined in greater detail in Communications 2 and 3, which will be devoted to our work on x-ray structure and magnetic determinations of the phase composition and structure of the catalysts described here.

From the results reported above it will be seen that dehydrogenation of i-C_3H_7OH goes to an appreciable extent only on catalysts containing more than 40 moles per cent of NiO. Table 4 gives the selectivity coefficients

for these catalysts; these are values of the ratio $C_3H_6 : C_3H_6 + H_2$, i.e. the contribution of dehydration to the over-all transformations of $i\text{-}C_3H_7OH$. Table 4 shows that with rise in the temperature of the decomposition of C_3H_7OH, K_s increases, i.e. dehydrogenation is accelerated to a greater extent than dehydration.

TABLE 4

Selectivity Coefficients (K_s)

(In all experiments, irrespective of the temperature of roasting, for Al_2O_3, $K_s = 1.00$; for NiO at 260° and 59.5% conversion $K_s = 0.01$)

Temperature of roasting (°C)	Composition of catalyst (moles %)										
	59,5 Al_2O_3 + 40,5 NiO				48,5 Al_2O_3 + 51,5 NiO				41 Al_2O_3 + 59 NiO		
	Temperature of experiment (°C)										
	245	260	275	290	245	260	275	290	260	275	290
400	—	0,88	0,90	0,96	—	0,36	0,62	0,77	0,43	0,67	0,75
600	0,95	0,98	0,97	—	—	0,74	0,84	0,89	0,67	0,77	0,87
750	0,91	0,96	0,97	—	0,70	0,70	0,76	—	0,54	0,70	0,77
900	—	—	—	—	—	0,35	0,40	0,51	—	0,26	0,63

Comparing selectivity coefficients of catalysts roasted at 400° with that of NiO, also roasted at 400°, we note that for mixed catalysts $K_s \gg K_s$ of NiO. For the mixed catalysts investigated the data on selectivity throw light on the phase composition and the changes that occur in it with increase in NiO content. As we pass from pure Al_2O_3 to a catalyst containing about 40 moles per cent of NiO, K_s remains constant and equal to unity. This indicates the absence of free NiO, because NiO dehydrogenates the alcohol and its K_s is zero; these catalysts must be one-phase systems. It may be expected that the catalyst containing 40 moles per cent of NiO, which has a weak dehydrogenating effect, will contain some free NiO arising from incomplete homogenization during the comparatively short period of thermal treatment. As analysis showed, with further increase in the amount of NiO added, its mole fraction exceeded that of Al_2O_3 and there is a change in K_s corresponding to this point. This change in selectivity is therefore associated with the appearance of a second phase in the catalysts, namely an NiO phase, the presence of which was confirmed by x-ray analysis. It should be noted that the chemical effect, i.e. change in K_s, is an important criterion in the determination of the phase composition of catalysts, particularly in cases in which physical methods do not give reliable results, as in the investigation [1] and in our work on the x-ray analysis of the catalyst containing 40.5 moles per cent of NiO.

The process that results in homogenization of the catalyst at a temperature as low as 400° and in the absence of free NiO (at contents below a certain limiting value) may be the formation of a spinel or of a solid solution in Al_2O_3 which also has a spinel lattice. This is not contradicted by the fact that spinels are formed from oxides at high temperatures [11]: a topochemical reaction in coprecipitated catalysts can proceed at the dehydration stage at considerably lower temperatures and may consist in the intermolecular dehydration of $Ni(OH)_2$ and AlOOH or $Al(OH)_3$.

Substantial confirmation of these views was obtained in experiments on an equimolecular mixture of separately prepared NiO and Al_2O_3, different portions of which were heated for 12 hours at 260°, 300°, 400° and 750°. Decomposition of $i\text{-}C_3H_7OH$ over these at 260° proceeded to the extent of 48, 58, 60, and 36%, respectively, and K_s increased rapidly with rise in roasting temperature and equaled 0.44, 0.76, 0.79, and 0.91, respectively. This indicates the combination of NiO, increasing in extent with rise in roasting temperature. It should be noted that K_s for the mixture roasted at 750° is identical with K_s for the coprecipitated catalyst containing 40.5% of NiO.

It is well known that in the preparation of a mixed $Ni - Al_2O_3$* catalyst the reduction of NiO proceeds readily and completely even at 300-320°. In the case of $NiO - Al_2O_3$ that has been subjected to thermal treatment the situation is quite different: catalysts containing up to 15 moles per cent of NiO are not reduced at all, even at 360° for 80-100 hours; catalysts of higher NiO content are either not reduced at all or are reduced only at the surface of the grains with formation of a thin layer of metal, as in the case of a catalyst of composition 68.5 $Al_2O_3 - 31.5$ NiO reduced at 350° and 425° for 30 hours. The formation of metal, which was evidenced

* As in original. Publisher's note.

by the character of the change in the color of the catalyst (the color did not change within the grain), was checked in experiments on the dehydrogenation of cyclohexane. Our experiments showed very clearly how difficult it is to reduce nickel in catalysts roasted at 400-750°; we think that this is to be explained by the strong linkage of the nickel atom in the spinel, as compared with nickel in NiO.

Calculation of the activation energy for dehydration gave the following results (the subscript indicates the temperature at which the catalyst was roasted): on Al_2O_3 $\epsilon_{400} = 18$ and $\epsilon_{750} = 13$ kcal/mole. When we pass to mixed catalysts ϵ remains almost constant for a given roasting temperature up to an NiO content of about 40 moles per cent, the average values being $\epsilon_{400} = 23$ and $\epsilon_{600-750} = 20$ kcal/mole, which indicates that the active centers in these catalysts are identical in nature and that the catalysts are identical in phase composition. In the case of catalysts containing 51.5 and 59 moles per cent of NiO, ϵ_{400} is 30 and $\epsilon_{600-750}$ is 27-28 kcal/mole. These results show that change in phase composition and selectivity is accompanied by increase in ϵ.

Hence, all the determinations made in the present investigation indicate that the formation of a spinel in $NiO - Al_2O_3$ catalysts prepared by coprecipitation is possible at temperatures as low as 400°.

SUMMARY

1. Study of the specific activities of $Al_2O_3 - NiO$ catalysts roasted at 400-750° for the decomposition of $i\text{-}C_3H_7OH$ showed that there is optimum activity with respect to composition for NiO contents ranging from 5-15 moles per cent.

2. It was shown that the selectivities of the catalysts studied depend on composition; over a wide range of NiO contents only dehydration occurs, which indicates absence of free NiO. Dehydrogenating power appears only in catalysts of high NiO content and indicates the formation of a free-NiO phase.

3. It was shown that in coprecipitated $NiO - Al_2O_3$ catalysts it is possible for the spinel $NiAl_2O_4$ to be formed at a temperature as low as 400° because of the intermolecular dehydration of the hydroxides.

4. The relation between specific surface and temperature of roasting was determined for these catalysts over the range 400-900°.

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DISTRIBUTION OF π-ELECTRON DENSITY AND INTERATOMIC DISTANCES

COMMUNICATION 4. SEMIEMPIRICAL EQUATIONS FOR CALCULATION PURPOSES

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In the five years that have elapsed since our first communications on this subject a mass of new experimental data on interatomic distances has accumulated. The most valuable information was obtained by spectroscopic methods of investigation and particularly by methods of microwave spectroscopy (radiospectroscopy) of gases, though they are applicable only to relatively simple polar molecules. As a result of improvements in technique, the accuracy of electron-diffraction investigations has risen considerably. Many new substances have been studied by x-ray analysis, but, as is well known, this method is not suitable for determining the positions of hydrogen atoms and, moreover, it is found that the determination of interatomic distances in solids gives, in general, somewhat low values as compared with the bond lengths in the free molecules. Other methods of studying interatomic distances, e.g. neutron diffraction, have not yet been developed sufficiently. Interatomic distances are determined by spectroscopic methods with absolute errors which are closer to 0.001• than to 0.01, whereas electron and x-ray diffraction methods are associated with absolute errors ranging mainly from 0.01 to 0.03.

Since our first calculations of π-electron charges of bonds, other possibilities have appeared for their calculation, and this has made it possible to compare results obtained in different ways and to check their agreement with one another [1,2]. There is no longer any necessity to present further proofs of the hypothesis of the nonintegral character of electron charges of bonds and of the possibility of calculating them from the results of physical investigations. We may now discuss only the improvement of our calculations. This is necessary not only to bring them into accord with new experimental data, but also for the sucessful development of the whole problem of electron charges of bonds, part of which is the problem of the relation of interatomic distances to π-electron charges of bonds.

In a general form this relation can be expressed [3] by the equation

$$l = L - \Delta^{\pi} A^{\pi},$$

in which l is the length of the given bond, L is the length of the standard σ-bond, A^{π} is the π-electron charge of the bond, and Δ^{π} is the specific shortening (contraction) of the bond produced by a π-electron charge equivalent to one π-electron. L and Δ^{π} are constants depending on the elements between which the bond is formed and sometimes also on the type of bond (e.g. the C–C bond). Hence, Equation (1) corresponds to a series of derived equations differing from one another in the values of the constants. The present paper is devoted to the calculation of these constants, and in the next communication we shall examine the π-electron charges of bonds met in organic compounds.

The C – C Bond. As the standard length of a C – C bond we shall take its length in diamond $L_{C-C} = 1.542$. For calculations of Δ^{π} we shall require the data in Table 1.

Substituting data for the C≡C bond in acetylene in Equation (1), we obtain $\Delta^{\pi}_{C\equiv C} = 0.131$ A/e.

• Interatomic distances are always given in Angstrom units, and electron charges of bonds are given in electrons.

Strictly speaking, we should take account of the effect of the σ-electron charge of the C – C bond on its length, if this charge differs from two electrons in value. In our earlier investigations we neglected this effect. It can be shown that there is justification for so doing. To estimate the shortening of C – C bonds due to σ-electron charges A^{σ} let us assume that it is proportional to $(A^{\sigma}-2)$. The total shortening of the C – C bond can then be expressed by the equation

$$L - l = \Delta^{\sigma}(A^{\sigma} - 2) + \Delta^{\pi}A^{\pi}. \qquad (2)$$

By the use of the data of Table 1 for ethylene, allene, and benzene we may obtain three equations containing two unknowns Δ^{σ} and Δ^{π}. Solving these in pairs we find that, on the average, $\Delta^{\sigma} = 0.006$ and $\Delta^{\pi} = 0.154$.

From this we may draw two important conclusions: 1) the effect of the σ-electron charges of C–C bonds on the reduction of the interatomic distances (taking account of the fact that $(A^{\sigma} - 2) \geq 0.55$ σ) is so small that it may be neglected; 2) Δ^{π}_{CC} for C≡C in acetylene on the one hand and the same quantity for the C=C bonds in ethylene and allene and the C=C bond in benzene on the other are numerically different. Since we neglect the effect of σ-electron charges on bond lengths, $\Delta^{\pi}_{C=C}$ can be calculated directly by substituting for L_{CC} and A^{π} from Table 1 in (1). We find $\Delta^{\pi}_{C=C} = 0.1554$ for ethylene, 0.1550 for allene, and 0.1523 for benzene, the average value still being 0.154.

It is natural to assume that the ≡C – C bond in propyne, the ≡C – C≡ bond in butadiyne, and other similar bonds will also differ in specific shortening from bonds of the first two types. We shall see that this is so. There then arises the question of whether Δ^{π}_{CC} for bonds of the type ≡C – C will not differ from that for bonds of the type ≡C – C≡. However, the fact that the shortening not only of these bonds, but also of the = C–C= bond in butadiene and of the $C_{ar} - C_{ar}$ bond in biphenyl is proportional to the number of π-electrons on the atoms forming the bond, irrespective of whether the atom-donors of π-electrons are to be found on both sides or only on one [10], justifies the treatment of all these bonds as a single group having a characteristic value of Δ^{π}_{CC}.

TABLE 1

Lengths and Electron Charges of C – C Bonds in Hydrocarbons

Compound	l*	σ***	π***
Acetylene	1,208 [4]	2,554	2,554 (2,27)****
Ethylene	1,330** [5]	2,256	1,364 (1,42)
Allene	1,309 [6]	2,363	1,500
Benzene	1,397 [7]	1,910	0,952 (0,95)

*It is necessary to distinguish between hypothetical equilibrium interatomic (internuclear) distances (in acetylene 1.201 [4]), which are identical for all isotopic varieties of the given compound, and average interatomic distances. In the great majority of cases interatomic distances of the second kind have been determined, and it is these that we shall use in our calculations. The differences between the two kinds of interatomic distances is not generally greater than 0.5%.

**For reasons that we shall consider in the next communication we take this value of the length of the C – C bond in ethylene, and not the value of 1.353, accepted in the literature [8].

***The σ- and π-electron charges were calculated by the author from heats of formation and frequencies [2, 9].

****For comparison purposes we give values of π-electron charges of these bonds in parentheses which were obtained from interatomic distances by calculations of low accuracy [3].

In view of the absence of reliable experimental data on the C – C bonds, in 2-butyne, for the calculation of Δ^{π}_{C-C} it is necessary to start from the interatomic distances in CH_3CN, in which $l_{CC} = 1.458$ and $l_{CN} = 1.157$ [11]. According to (1), $\Delta^{\pi}_{CC} = (L_{CC} - l_{CC})/A^{\pi}_{CC}$. It is clear that $A^{\pi}_{CC} = 4 - A^{\pi}_{CN}$, and $A^{\pi}_{CN} = (L_{CN} - l_{CN})/\Delta^{\pi}_{CN}$. The values of L_{CN} and Δ^{π}_{CN} are given below; using these, we obtain $\Delta^{\pi}_{C-C} = 0.126$.

The C – H Bond. In CH_4 $L_{CH} = 1.093$ [13]. In acetylene $l_{CC} = 1.058$ [4] and $A^{\pi}_{CH} = 0.723\pi$ [2]. Hence $\Delta^{\pi}_{CH} = L_{CH} - l_{CH})/A^{\pi}_{CH} = 0.048$.

The C – N Bond. In CH_3NH_2 $L_{CN} = 1.474$ [14]. In HCN $l_{CH} = 1.061$ and $l_{CN} = 1.157$ [15]. Hence, $A^{\pi}_{CH} = L_{CH} - l_{CH})/\Delta^{\pi}_{CH} = 0.667\pi$; $A^{\pi}_{CN} = 4 - A^{\pi}_{CH} = 3.333\pi$; $\Delta^{\pi}_{CN} = (L_{CH} - l_{CN})/A^{\pi}_{CN} = 0.095$. The experimental data are inadequate for us to differentiate between $\Delta^{\pi}_{C\equiv N}$, $\Delta^{\pi}_{C=N}$, and Δ^{π}_{C-N} in the way that we have done for C – C bonds. Also, the calculation of $\Delta^{\pi}_{C=N}$ and Δ^{π}_{C-N} is not so simple because of the increase in the π-electron cloud in these bonds due to the "free" pair of electrons on the nitrogen atom.

The C – O and C – S Bonds. In CH_3OH $L_{CO} = 1.428$ [16], and in CH_3SH $L_{CS} = 1.818$ [17]. In CO_2 $l_{CO} = 1.162$ [18], and in CS_2 $l_{CS} = 1.554$ [19]; in each of these compounds there are two π-electrons per bond. Hence, $\Delta^{\pi}_{CO} = (L_{CO} - l_{CO})/2 = 0.133$, and $\Delta^{\pi}_{CS} = 0.132$. It is possible that the Δ^{π} values for C = O and C = S bonds on the one hand and C – O and C – S bonds on the other may differ somewhat, but it is as yet impossible to verify this.

The C – F, C – Cl, C – Br, and C – I Bonds. In CH_3F $L_{CF} = 1.385$ [20]. As neither fluoroacetylene nor cyanogen fluoride are known, for the calculation of Δ^{π}_{CF} we use data for formyl fluoride HCOF, for which it has been shown by electron diffraction that $l_{CF} = 1.351 \pm 0.013$ and $l_{CO} = 1.192 \pm 0.011$ [21]. We can scarcely suppose that the π-electron charge of the C – H bond in this compound is greater than in benzene, for which it has been found that $A^{\pi}_{CH} = 0.048\ \pi$ [9]. If we assume that for HCOF $A^{\pi}_{CH} = 0.05\ \pi$, in further calculations our error will not be greater than that due to the inaccuracy in the determination of the lengths of the C – F and C – O bonds. A^{π}_{CO} is readily calculated from (1); hence $A^{\pi}_{CF} = 2 - (A^{\pi}_{CH} + A^{\pi}_{CO})$ and $\Delta^{\pi}_{CF} = (L_{CF} - l_{CF})/A^{\pi}_{CF} = 0.189$. All calculations of A^{π} and l for C – F bonds can, of course, only be approximate.

In the corresponding CH_3X compounds [22], $L_{CCl} = 1.782$, $L_{CBr} = 1.938$, and $L_{CI} = 2.140$. There are two possible ways of calculating Δ^{π}_{CCl}. We may take the interatomic distances in dichloroacetylene $l_{CC} = 1.195$ and $l_{CCl} = 1.640$, which we used previously [23], or in ClCN $l_{CCl} = 1.629$ and $l_{CN} = 1.163$ [22]. In both cases $\Delta^{\pi}_{CCl} = 0.210$. In BrCN [22] $l_{CBr} = 1.790$ and $l_{CN} = 1.159$, and in ICN [22] $l_{CI} = 1.995$ and $l_{CN} = 1.159$, whence $\Delta^{\pi}_{CBr} = 0.188$ and $\Delta^{\pi}_{CI} = 0.185$.

The N – N and N – O Bonds. For these bonds we must assume [23] the not very reliable values of $L_{NN} = 1.46$ and $L_{NO} = 1.37$. For the calculation of Δ^{π}_{NN} we use the N ≡ N bond in the nitrogen molecule, $l_{NN} = 1.100$ [24], in the formation of which four π-electrons take part. We then have $\Delta^{\pi}_{NN} = (1.46 - 1.100)/4 = 0.090$. In hydrazoic acid HNN'N" $l_{NN'} = 1.240$ and $l_{N'N''} = 1.134$ [25]. Hence $A^{\pi}_{NN'} + A^{\pi}_{N'N''} = 2.444 + 3.622 = 6.066\ \pi$, i.e. the three atoms provide six π-electrons, evidently N one, N" two, and the middle N' three. Nitrous oxide ONN has a similar structure, O playing the part of HN in hydrazoic acid. In nitrous oxide $l_{NO} = 1.191$ and $l_{NN} = 1.126$ [22]. Whence $A^{\pi}_{NN} = (L_{NN} - l_{NN})/\Delta^{\pi}_{NN} = 3.711\ \pi$; $A^{\pi}_{NO} = 6 - A^{\pi}_{NN} = 2.289\pi$; $\Delta^{\pi}_{NO} = (L_{NO} - l_{NN})/A^{\pi}_{NO} = 0.078$.

Table 2 gives a summary of the results of our calculations. Substituting the values of L and Δ^{π} from this table in Equation (1) we obtain derived equations for the calculation of the π-electron charges of bonds in organic compounds. The accuracy of these calculations will depend on the reliabilities of the values of L, Δ^{π} and l used. Without going into a detailed analysis we may state, in general, that with the exception of the case of the C – F bond, error in the determination of L and Δ^{π} will affect the accuracy of the results of the calculation of π-electron charges less than error in l, if this is determined with an absolute error of ± 0.01 or more. As the error in most of the data on interatomic distances is just of this order, in the last column of the table we give values of $\epsilon_{A\pi}$, the absolute error in the determination of the π-electron charge corresponding to an error in the determination of bond length of $\epsilon_l = \pm 0.01$.

• In the preceding communication [1] we referred to Scherr's equation for C – C bonds, which differs from ours only in that $L_{CC} = 1.525$ and $\Delta^{\pi}_{CC} = 0.1398$. In a later paper Scherr [12] proposed an equation in which $L_{CC} = 1.54$ and $\Delta^{\pi}_{CC} = 0.1385$; he confined himself to a single equation for the bonds C =C, C_{ar} —— C_{ar}, and C–C, but Δ_{CC} was very close in value to the arithmetic mean of $\Delta^{\pi}_{C=C}$ and Δ^{π}_{C-C} in our equations.

Our equations, though applicable to the bulk of data on interatomic distances, is nevertheless not applicable in every case. We have already stated that the determination of interatomic distances in solids gives lower values than determinations in the gas phase. It is clear that in such cases some corrections must be made in the appropriate equations in order to improve the accuracy of our calculations (see the next paper). It is known that in the halomethanes all the interatomic distances become shorter as halogen atoms accumulate in the molecule. Here again it is necessary to make a correction in calculations on compounds of the type of tetrahaloethylene or phosgene. As, however, the laws of this phenomenon are not yet clear, it is not yet possible to propose a rational way of determining the correction. Also, the field of application of the proposed equations is limited in another respect. However small the influence of σ-electron charges of bonds on interatomic distances may be, it will become relatively greater as the π-electron charges become smaller. Thus, according to our calculation [9], in benzene $A^{\pi}_{CH} = 0.048\ \pi$, which gives $l_{CH} = L_{CH} - \Delta^{\pi}_{CH} A^{\pi}_{CH} = 1.091$, whereas it has been found that [7] $l_{CH} = 1.084 \pm 0.005$, which corresponds to a π-electron charge of $A^{\pi}_{CH} = 0.19 \pm 0.10\ \pi$. It is evident that, for A^{π}_{CH} = about $0.1\ \pi$ and less, Equation (1) for C – H bonds can no longer be regarded as reliable.

TABLE 2

Lengths of Standard σ-Bonds and Specific Contractions

Bond	L	Δ^{π}	Δ^{π} [23] *	$\pm\varepsilon_{A^{\pi}}$
C≡C	0,542	0,131	0,149	0,08
C=C		0,154		0,06
C—C		0,126		0,08
C—H	1,093	0,048	0,042	0,21
C—N	1,474	0,095	0,10	0,11
C—O	1,427	0,133	0,15	0,08
C—S	1,818	0,132	—	0,08
C—F	1,385	0,189	—	0,05
C—Cl	1,782	0,210	0,166	0,05
C—Br	1,938	0,188	0.16	0,05
C—I	2,140	0,185	0,13	0,05
N—N	1,46	0,090	0,09	0,11
N—O	1,37	0,078	0,08	0,13

*For comparison, in this column we give values of Δ^{π} calculated previously by the author [23] on the basis of old data on interatomic distances.

SUMMARY

1. Calculations were made of the constants occurring in semiempirical equations expressing the relation of interatomic distances to the π-electron charges of bonds in organic compounds.

2. It was shown that in the case of C – C bonds changes in σ-electron charge have relatively little effect on interatomic distances.

3. It was noted that a nitrogen atom can act as a donor of three π-electrons.

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DISTRIBUTION OF π-ELECTRON DENSITY AND INTERATOMIC DISTANCES

COMMUNICATION 5. π-ELECTRON CHARGES OF BONDS IN ORGANIC COMPOUNDS

G. V. Bykov

The way in which the equations proposed in the preceding communication [1] for the calculation of π-electron charges of bonds and interatomic distances is applied requires no explanation. We shall therefore examine only a few fundamentally important examples of the application of these equations in the determination of the structures of molecules and then give a survey of the π-electron charges of bonds typical for organic compounds; we shall discuss various hypotheses advanced in explanation of the regularities observed in interatomic distances.

Interatomic Distances in Allene and Ethylene. For allene it was at first found that $l_{CC} = 1.330$ (all interatomic distances in Angstrom units) and $l_{CH} = 1.087$ [2]. New results have been obtained recently: $l_{CC} = 1.30 \pm 0.005$ and $l_{CH} = 1.08$ [3]. As regards the length of the C – C bond, its value has been confirmed and determined with greater accuracy by Stoicheff [4], who obtained $l_{CC} = 1.309 \pm 0.001$. Stoicheff has only one equation for the calculation of l_{CH} and ∠HCH, and he therefore assumes that $l_{CH} = 1.07 \pm 0.01$. On the basis of Stoicheff's data we may calculated l_{CH} for the C – C bond as follows: from the equation

$$l_{CC} = 1{,}542 - 0{,}154\, A^{\pi}_{CC} \qquad (1)$$

we find $A^{\pi}_{CC} = 1.513\,\pi$. In allene $2A^{\pi}_{CC} + 4A^{\pi}_{CH} = 4$ π-electrons, and therefore $A^{\pi}_{CH} = 0.243\,\pi$, whence, by the equation

$$l_{CH} = 1{,}093 - 0{,}048\, A^{\pi}_{CC} \qquad (2)$$

we obtain $l_{CH} = 1.081$, which is in close agreement with one of the three values cited above.

For ethylene it was found spectroscopically that $l_{CC} = 1.330$ and $l_{CH} = 1.087$ [2], and later $l_{CC} = 1.353$ and $l_{CH} = 1.071$ [5], and also $l_{CC} = 1.344$ [4]. From the heat of formation of ethylene and the frequency of the symmetrical vibration of its C – H bond we calculated the π-electron charges of bonds in this compound: $A^{\pi}_{CC} = 1.364\,\pi$ and $A^{\pi}_{CH} = 0.159\pi$ [6]. In the calculation of the numerical coefficient of A^{π}_{CC} in Equation (1) we used the cited value of A^{π}_{CC} in ethylene, and in an independent calculation from data for benzene and allene only, according to the scheme given in the preceding communication, we obtained a value of 0.1536 ± 0.0014 for the coefficient. For ethylene we then obtain $l_{CC} = 1.542 - (0.1536 \pm 0.0014) \times 1.364 = 1.332 \pm 0.002$. Calculation by Equation (2) gives $l_{CH} = 1.085$. Hence, our calculation definitely favors the earlier determination of the interatomic distances in ethylene and is almost exactly in accord with Thompson's results: $L_{CC} = 1.331$ and $l_{CH} = 1.085$ [7].

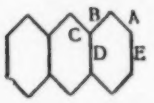
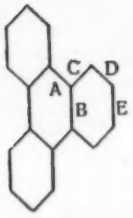
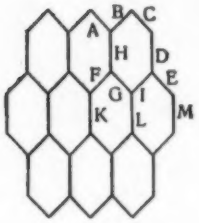
π-Electron Charges of Bonds in Polycyclic Aromatic Hydrocarbons. We have already stated [1] that x-ray diffraction gives somewhat low values of interatomic distances. A good example is found in benzene. The spectroscopic method gives $l_{CC} = 1.397 \pm 0.001$ [8], and the x-ray method about 1.392 [9]. In the calculation from Equation (1) this difference leads to a difference of 0.03 π-electrons, which can be of real significance in the calculation of the total π-electron charge of C – C bonds in polycyclic aromatic systems. Hence, in the calculation of A^{π}_{CC} from x-ray data a certain correction is required. Calculating the specific contraction Δ^{π}_{CC} as

we did in [1] while using the value $l_{CC} = 1.392$ for benzene, we obtain $\Delta^{\pi}_{CC} = 0.158$, the corresponding equation being

$$l_{CC} = 1{,}542 - 0{,}158\, A^{\pi}_{CC}. \qquad (3)$$

TABLE 1

Lengths and π-Electron Charges of C – C Bonds in Polycyclic Aromatic Hydrocarbons

Compound	Bond	l	$A^{\pi}(l)$	A^{π} [11]	$A^{\pi}(l) - A^{\pi}$ [11]
1	2	3	4	5	6
Anthracene 	*A*	1,370	1,09	1,094 (1,07)	0,00
	B	1,423	0,75	0,777 (0,80)	—0,03
	C	1,396	0,92	0,867 (0,90)	+0,05
	D	1,436	0,67	0,603 (0,51)	+0,07
	E	1,408	0,85	0,921 (0,95)	—0,07
Triphenylene 	*A*	1,47	0,46	0,575	—0,11
	B	1,435	0,68	0,683	0,00
	C	1,39	0,96	0,8 4	+0,12
	D	1,375	1,10	1,043	+0,06
	E	1,385	0,99	0,969	+0,02
Ovalene 	*A*	1,404	0,87	0,867	0,00
	B	1,441	0,64	0,753	—0,11
	C	1,345	1,25	1,134	+0,12
	D	1,433	0,69	0,762	—0,07
	E	1,403	0,88	0,796	+0,08
	F	1,428	0,72	0,680	+0,04
	G	1,426	0,73	0,667	+0,05
	H	1,435	0,68	0,637	+0,04
	I	1,416	0,80	0,664	+0,14
	K	1,461	0,51	0,641	—0,13
	L	1,442	0,63	0,662	—0,03
	M	1,383	1,01	1,097	—0,09

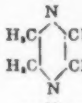
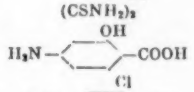
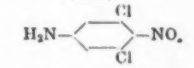
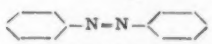
The third column of Table 1 lists experimentally determined interatomic distances [10], and the fourth lists π-electron charges of bonds calculated by us from the data in the third column by Equation (3); the fifth column lists values of π-electron charges according to Scherr's data [11], and in parentheses in the same column are given values according to Bagdasar'ian's [12]. As will be seen from the last column, which gives the difference between our results and those of Scherr, only in two cases does this difference exceed an absolute error of $\epsilon_A = \pm 0.12\,\pi$ in the calculation of A^{π}, corresponding to an absolute error of $\epsilon_l = \pm 0.02$ in the experimental values of l.

π-Electron Charges of Bonds Formed with Nitrogen. In the second communication of this series [13] on the basis of a calculation of π-electron charges in some nitrogen-containing compounds we suggested • that the "free pairs" of electrons of nitrogen atoms attached directly to atom donors of π-electrons participate partially or entirely in these bonds and supplement their π-electron cloud. New data may now be cited in favor of this suggestion (see Table 2).

• Two of the working hypotheses advanced at that time, namely that the π-electron charges in propyne and analogous compounds are extended also to the C – H bonds of the methyl group and that for compounds with contiguous C=C bonds a special scheme of calculation is necessary, are now rejected by the author.

TABLE 2

π-Electron Charges of Bonds in Nitrogenous Organic Compounds

No.	Compound	Bond	l	Method* and literature reference	A^{π}
1	H_3C-N-C	C=N	1,167	S [14]	3,23
		C—N	1,427		0,49
2	$HN=C=O$	C=N	1,207	S [15]	2,81
		C=O	1,171		1,92
3	$HN=C=S$	C=N	1,216	S [16]	2,72
		C=S	1,561		1,95
4	$H_3C-N=C=S$	C=N	1,22	S [17]	2,68
		C—N	1,47		0,00
		C=S	1,56		1,95
5	$(CH_3SO_4)_3C-C=N-CH_3$	C=N	1,154	X[18]	3,37
		C—N	1,426		0,51
		C=C	1,342		1,30
		=C—S	1,726		0,70
6		$C_{ar}=N_{ar}$	1,340	S [19]	1,41
		$C_2=C_3$	1,390		0,96
7		$C_{ar}=N_{ar}$	1,31	X [20]	1,73
		$C_{ar}=C_{ar}$	1,44		0,66
		$C_{ar}-C$	1,50		0,33
8		$C_{ar}=N_{ar}$	1,319	X [21]	1,63
9	CH_3CONH_2	C—N	1,36	E [22]	1,20
		C=O	1,21		1,63
		C—C	1,53		0,10
10	$(H_2N)_2C=O$	C—N	1,335	X [23]	1,46
		C=O	1,262		1,24
11	$(CONH_2)_2$	C—N	1,315	X [24]	1,67
12	$(CSNH_2)_2$	C—N	1,308 / 1,285	X [25]	1,75 / 1,99
13		$C_{ar}-N$	1,39	X [26]	0,88
14		$C_{ar}-NH_2$	1,37	X [27]	1,10
15		$C_{ar}-N$	1,41	X [28]	0,78
		N=N	1,23		2,56
16	CHO—NH—NH—CHO	C—N	1,32	X [29]	1,62
		N—N	1,38		0,89
		C=O	1,21		1,63

*S, spectroscopic; X, x-ray diffraction; E, electron diffraction.

It is considered that in methyl isocyanide the nitrogen and carbon atoms each give the system one π-electron. However, the total π-electron charge of the molecule, as calculated from interatomic distances, is greater than this by almost two π-electrons. That this increase is due to the nitrogen atom and not the carbon can be inferred from the next three examples (No. 2-4), in which the π-electron charges of the C=O and C=S bonds have approximately normal values, i.e. about two π-electrons, whereas the π-electron charges of the C—N bonds are considerably higher. The next compound (No. 5) is also of this type. If we make a rough estimation of the contribution made by the central carbon atom attached to sulfur to the π-electron charge of the C = C bond as 0.5 ± 0.5 π, then the total charge of this bond and two C — N bonds would appear to be 3.5 ± 0.5 π-electrons, whereas calculation from interatomic distances gives 5.18 π. Although this value must be regarded as somewhat high because the interatomic distances were determined by the x-ray method, there can be no doubt that the nitrogen atom is the donor of not one, but at the least two π-electrons.

As can be seen from the next three examples (No. 6-8), nitrogen atoms of heterocycles are also donors of more than one π-electron. Thus, in s-triazine, calculation indicates that the π-electron cloud is formed from

almost ten electrons, i.e. four electrons more than is required by the usual valence scheme. Examples No. 9-12 show that the NH_2 group in amides is also a donor of π-electrons. In this case the nitrogen atom provides the system with about one π-electron. The high values of π-electron charges of C–N bonds in compounds in which the NH_2 group is attached to the aromatic ring (the next two examples) indicate the same state of affairs.

TABLE 3

π-Electron Charges of Bonds in Organic Compounds

Bond	A^{π}	Bond	A^{π}	Bond	A^{π}
$-C\equiv C-$	2,52—2,56	$=C=O$	1,95—2,1	$\equiv C-Cl$	0,69—0,73
$=C=C=$	1,8—2,0	$\diagup C=O$	1,5—1,6	$=C-Cl$	0,4
$=C=C\diagup$	1,4—1,5	$=C-O-$	0,2	$\approx C_{ar}-Cl$	0,46
$\diagup C=C\diagup$	1,3—1,4	$\approx C_{ar}-O-$	0,3	$\equiv C-Br$	0,77—0,79
$\approx C_{ar}=C_{ar}\diagdown$	0,95(benzene) 0,5—1,3	$=C=S$	1,95	$=C-Br$	0,2—0,4
$\equiv C-C\equiv$	1,40	$\diagup C=S$	1,2	$\approx C_{ar}-Br$	0,41
$\equiv C-C=$	1,0	$=C-S-$	0,3	$\equiv C-I$	0,78
$\equiv C-C_{ar}\approx$	1,0	$\approx C_{ar}-S-$	?	$=C-I$	?
$=C-C=$	0,57—0,63	$-C\equiv N$	3,27—3,34	$\approx C_{ar}-I$	?
$=C-C_{ar}\approx$	0,67	$=C=N-$	2,7—3,4	$=N\equiv N$	3,7
		$:C=N-$	3,23*	$\equiv N=N-$	2,4
$\approx C_{ar}-C_{ar}\approx$	0,43	$\diagup C=N-$	1,94 (oximes)	$-N=N-$	2,6
$\equiv C-C\diagup$	$\geqslant 0,67$	$\approx C_{ar}=N_{ar}\approx$	1,4—1,7	$\approx N_{ar}=N_{ar}\approx$	?
$\diagdown$		$=C-N\diagup$	1,2—1,7	$\diagup N-N\diagup$	$\leqslant 0,9$ **
$=C-C\diagup$	?			$\equiv N=O$	2,29 (isocyanates)
$\diagdown$		$\approx C_{ar}-N\diagdown$	0,9—1,1	$\geqslant N=O$	1,9 (nitro group)
$\approx C_{ar}-C\equiv$	0,06	$\diagup C-N=$	$\leqslant 0,5$	$-N=O$	?
$\equiv C-H$	0,67—0,73			$=N-O-$	$\geqslant 0,1$
$\geqslant C-H$	$\leqslant 0,16$	$=C-F$	$>0,2$		
$\approx C_{ar}-H$	$\leqslant 0,05$	$\approx C_{ar}-F$	0,56		

*(isocyanides).

**See No. 16 in Table 2.

In azobenzene (No. 15), nitrogen atoms evidently again provide the system with more than one π-electron each. A particularly interesting example is 1,2-diformylhydrazine. If we consider that only the carbon and oxygen atoms are donors of π-electrons, then the total π-electron charge of bonds in this compound must be four π-electrons, whereas it is actually almost twice as great; moreover, the π-electron charge provided by the nitrogen atoms is distributed not only over the C – N bonds, but also over the N–N bond, which is shortened considerably; this would not occur if the nitrogen atoms were not themselves donors of π-electrons.

π-Electron Charges of Bonds in Organic Compounds. The electron charges of analogous bonds in organic compounds vary within more or less narrow limits. It is noticeable that the lower the electronegativities of the elements attached to the atoms of a bond, the greater the π-electron charge of the bond. Thus, the highest π-electron charge is possessed by, e.g., the C = C bond in ethylene, but not in its derivatives, or the C = O bond in formaldehyde, but not in acids. In Table 3 we summarize the results of our calculations of the π-electron charges of bonds in organic compounds, the calculations being based on data in the literature on interatomic distances. 1 When two values are given, the greater generally refers to the simplest hydrogen compound in which the bond occurs.

Hypotheses Advanced in Explanation of Regularities Observed in Interatomic Distances. At one time the resonance scheme was in extensive use; according to this, if a bond "resonates" between single and double bonds

its length will be intermediate between the extreme values. For "nonresonating" molecules it was necessary to introduce supplementary ideas, in particular the concept of hyperconjugation. However, even then there remains the difficulty of explaining the lengths of bonds in which only one atom is a donor of π-electrons (a fact to which we drew attention in the first paper of this series [30]). Hence, resonance theory is incapable of giving even a qualitative interpretation from a unified viewpoint of peculiarities observed in interatomic distances, which is in fact acknowledged by Wheland in his recent monograph [31]. In the treatment of "resonating" molecules a fundamental defect comes to light as soon as we pass from the qualitative formulation given above to calculations. It is indeed always possible to select real or imaginary bonds of given characteristics which, when averaged in definite proportions, will give the length of a given bond and will enable us to determine the percent "double-bond character" of the bond. Huckel [32], in criticizing the well known method of Pauling for carrying out this operation, asked quite justifiably why there is any need to calculate percent double-bond charcter, which has no definite physical meaning. Hence, the qualitative "explanations" of resonance theory consist in an expression in the peculiar language of this theory of the results of empirical generalizations, and the quantitative treatment has a quasitheoretical character.

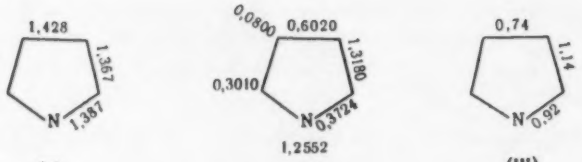
Relationships are established between bond order and bond length. As, however, bond order, in its turn, corresponds in some degree with electron density, there are grounds for the view that interatomic distances depend on the distribution of electron density. However, in the theory of bond order this relation is a very indefinite one, for the bond order changes according to the method of calculation, and in the graphical methods of establishing a relationship between bond order and bond length we can discover the same defects as in the method of "double-bond character." We will make a comparison with our theoretical scheme. Instead of the rather obscure concept of bond order, we shall use the π-electron charge of the bond, a concept which can be interpreted in one way only. A very simple direct relationship has been established between the length of a bond and its π-electron charge, and there is therefore no need for any intermediary such as "bond order." Since π-electron charge is an additive quantity, we can calculate interatomic distances in a purely theoretical manner, as shown at the beginning of this paper for the case of the C – H bond in allene.

An attempt is being made to interpret the regularities observed in interatomic distances on the basis of the view that these distances depend on valence states (hybridization of orbitals associated with the atoms. However, as can be very readily seen from Tatevskii's theoretical scheme [33], no convincing arguments can be advanced in favor of this suggestion. Actually, Tatevskii's proposed classification of bonds in hydrocarbons, which is based on the multiplicity of the bonds and the valence states of the atoms that they link together, can, as we have pointed out previously [30], serve as a prerequisite for the explanation of the regularities observed in interatomic distances, but not as the explanation itself. It in no way answers the question of the intrinsic relation between bond lengths and the valence states of atoms; nor does it provide any explanation of why there is a variation in the properties of bonds belonging to the same subtype, i.e. formed by the same atoms in the same valence states. It gives no explanation of what, from the point of view of valence states, is meant by "mutual effects of atoms," to which attention must be drawn at this point. In particular cases Tatevskii is compelled to go outside the scope of his phenomenological scheme, assuming fractional π-bonds (one half of a π-bond in benzene and one-third of a π-bond in graphite [33, p. 103]) and assuming also, admittedly as a hypothesis which he himself makes no use of, a certain fraction of a π-bond in the central C – C bond of butadiene [33, pp. 101, 104]. As Tatevskii showed, the detailed classification of bonds as types and subtypes makes it possible to construct satisfactory additive schemes for the calculation of some physicochemical properties of hydrocarbons, but valence states play no part in calculations according to these schemes. I consider that this classification can find a theoretical basis only in the concepts of fractional σ- and π-electron charges of bonds.

Another attempt to explain the regularities observed in interatomic distances is based on the view that increase in the difference in the electronegativities of the linked atoms leads to a shortening of the bond. Thus, the C – H bond in acetylene is shorter than the methane bond because the electronegativity of acetylene carbon is higher than that of alkane carbon [34]. Use is made of the well-known equation of Schomaker and Stevenson [35], $l_{xy} = r_x + r_y - k\,|E_x - E_y|$, which is applicable in the calculation of the lengths of σ-bonds from the covalent radii r and the electronegativities E (k is an empirical constant). Nevertheless, the concept of electronegativities in this form could not be used for the extensive interpretation and calculation of interatomic distances in unsaturated compounds. This is understandable, because, as follows from our scheme, bond length is determined mainly by the electron charge of the bond. π-Electron charges can be calculated, as we have shown [36], not only from interatomic distances, but also from electronegativities of atoms, though on the basis of quite

different considerations. We have to admit the possibility, however, that the difference in the electronegativities of the atoms forming a bond may affect the bond length. In the future, therefore, our theoretical scheme may require some refinement in this direction.

Finally, we must refer to a hypothesis which approaches ours more closely than any other. According to this hypothesis, interatomic distances depend on the π-electron charges of bonds, but these form only a part of the general π-electron cloud of the molecule, and the remaining part is distributed over the atoms. This view is held by Bak [37], who has attempted to calculate (by a very artificial scheme) the distribution of π-electron charges in pyridine, pyrrole, and furan molecules from the interatomic distances. By way of example we give the interatomic distances (I) in pyrrole and the π-electron charges according to Bak's data (II) and to ours (III).



(I) (II) (III)

As will be seen, Bak also assumes partial participation of the "free pairs" of electrons of the nitrogen in the bonds which it forms. In the case of carbon, however, there is no need to attribute π-electron charges to atoms. This would be an unjustifiable complication of the whole problem, and it is all the more superfluous in that, without this assumption, satisfactory results can be obtained with our scheme in the calculation of interatomic distances and the distribution of π-electron charges. Moreover, what is assumed to be the π-electron charges of carbon atoms can be interpreted (in pyrrole, for example) as π-electron charges of C – H bonds.

SUMMARY

1. The lengths of C – H bonds in allene and ethylene and of C – C bonds in ethylene were calculated.

2. The π-electron charges of C – C bonds in anthracene, triphenylene, and ovalene were calculated. A comparison was made with Scherr's calculations.

3. It was shown that, when a nitrogen atom forms a bond with an atom-donor of π-electrons, the free pair of electrons almost always passes, wholly or partially, into the bond and increases its π-electron charge.

4. A table is given of π-electron charges in organic compounds.

5. A discussion is given of various hypotheses which have been advanced for the explanation of the regularities observed in interatomic distances.

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NOTE

After this and the preceding communication had been submitted for publication, papers appeared which directly or indirectly confirmed the scheme of calculation, and therefore the theoretical scheme, advanced by the author.

1. Bartell and Bonham [38] made a new electron-diffraction investigation of the structure of ethylene; they give two pairs of values: $l_{CC} = 1.330 \pm 0.003$, $l_{CH} = 1.074 \pm 0.005$ and $l_{CC} = 1.334$, $l_{CH} = 1.085$, whereas, according to our calculation (see above), $l_{CC} = 1.332 \pm 0.002$ and $l_{CH} = 1.085$.

2. Stoicheff [39] found that in butatriene $H_2C'C''C'''C''''H_2$ $l_{C''C'''} = 1.284 \pm 0.006$; and he assumed that, as in allene, $l_{C'C''} = l_{C'''C''''} = 1.309 \pm 0.003$. This view is equivalent to the assumption that $A^{\pi}_{C''C'''} = 2\pi$. As the atoms C'' and C''' are donors of two π-electrons, for the calculation of the length of this bond it is necessary [1] to use the equation

$$l_{CC} = 1{,}542 - 0{,}131\, A^{\pi}_{CC},$$

and substituting $A^{\pi}_{CC} = 2\pi$, we find that $l_{CC} = 1.280$.

3. By the use of Equation (1) we may calculate beforehand the lengths of C – C bonds in the cyclopentadienyl and tropylium ions $C_5H_5^-$ and $C_7H_7^+$. In benzene the C –H bond is to be assigned 0.05 of a π-electron [6]. We shall assume this value of A^{π}_{CH} for both ions, which is very probable in the case of tropylium when we consider the closeness (almost coincidence) of the frequencies of the symmetrical valence vibrations of C – H bonds in it and in benzene [41]. Each ion has six π-electrons. Hence, in $C_5H_5^-$ the C – C bond has $A^{\pi}_{CC} = 1.150\ \pi$, and in $C_7H_7^+$ $A^{\pi}_{CC} = 0.807\ \pi$. Substituting these values in (1), we find $l_{CC} = 1.365$ in $C_5H_5^-$ and $l_{CC} = 1.418$ in $C_7H_7^+$.

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ω,ω'-IMINO DICARBOXYLIC ACIDS AND SOME OF THEIR DERIVATIVES

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The higher normal dicarboxylic acids find extensive application as starting materials for the preparation of synthetic resins, fibers, plasticizers, oil additives, etc. In recent years there has been a growing interest in dicarboxylic acids containing a hetero atom (group) in the chain; i.e. $A[CH_2)_nCOOH]_2$, in which A = S, O, SO_2, NH, etc. In several cases, such compounds, being more accessible than alkanedioic acids having the same number of carbon atoms, can serve as substitutes for these. Moreover, the introduction of the hetero atom makes it possible to make substantial modifications in the properties of the products. In particular, compounds of this type in which A = S, S_2, SO, SO_2, and S_2O_2 and $\underline{n}$ = 4, 6, and 8 have been prepared from the now readily available ω-chloro carboxylic acids [1, 2]. There are references in patents to the possibility of preparing nitrogenous resins from derivatives of 3,3'-iminodipropionic acid [3, 4].

In this paper we describe the synthesis of dicarboxylic acids of the type $A[(CH_2)_n COOH]_2$, in which A = = NH and $\underline{n}$ = 6, 8, and 10 and their N- and O-derivatives. Among compounds of this type, iminodiacetic, 3,3'-iminodipropionic, and 7,7-iminodiheptanoic acids have been described in the literature [5]. The last of these acids was prepared from pimelonitrile.

Imino dicarboxylic acids are generally prepared by reaction between amino acids and halo carboxylic acids or by the ammonolysis of the corresponding halo acids with aqueous ammonia. The higher ω,ω'-imino dicarboxylic acids have received little study until now because of the inaccessibility of the ω-chloro acids. We synthesized ω, ω'-imino dicarboxylic acids both by reaction between ω-chloro carboxylic acids and ammonia and by reaction of ω-chloro acids with ω-amino acids in presence of ammonia (in slight excess). The ω-chloro carboxylic acids were prepared by hydrolysis of the corresponding α,α,α,ω-tetrachloroalkanes with nitric acid of sp. gr. 1.52 [6]. The reactions were carried out without the application of heat. In the ammonolysis of ω-chloro carboxylic acids, not only the imino acids, but also the corresponding ω-amino acids were isolated.

Imino dicarboxylic acids are sparingly soluble in water and organic solvents; for purification they were converted into their soluble ammonium salts, which were then hydrolyzed at the boil (removal of ammonia). By reaction between ethyl 7-chloroheptanoate and methylamine we obtained diethyl 7,7'-(methylimino)diheptanoate. Hydrolysis of this ester led to the N-methyl imino acid, which was soluble in water.

The preparation of derivatives of the imino dicarboxylic acids presented some difficulties associated with the poor solubility of these acids and their multifunctionality. Thus, an attempt to prepare 7,7'-(methylimino) heptanoic acid by methylation of the imino acid with dimethyl sulfate resulted in a difficultly separable mixture of products. The ω,ω'-imino dicarboxylic acids were converted into the hydrochlorides of their diethyl esters in the usual way.

The reactions of 7,7'-iminodiheptanoic acid were investigated in some detail. We prepared the following derivatives: the diethyl ester, the N-acetyl derivative, the N-methyl derivative of the acid and its ester, the monoethyl ester of the monoamide, the hydrochloride of the diamide, and the hydrochloride of the monoethyl ester of the N-methyl derivative.

EXPERIMENTAL

1. 7,7'-Iminodiheptanoic Acid

a) A mixture of 20 g of 7-chloroheptanoic acid and 100 ml of 13% aqueous ammonia was heated at 100°

for three hours in an autoclave. When ammonia was removed completely from the reaction mixture, a precipitate of 7,7'-iminodiheptanoic acid formed, and this was filtered off and washed with water; yield 6.1 g (37%). Repeated dissolution in ammonia and precipitation by removal of ammonia gave an imino acid of m.p. 215°.

Found %: C 61.43; 61.67; H 10.08; 10.10; N 5.22; 5.33 $C_{14}H_{27}O_4N$. Calculated %: C 61.50; H 9.95; N 5.12.

From the filtrate remaining after the isolation of the imino acid we obtained 9.3 g (52%) of 7-aminoheptanoic acid free from chloride ion.

b) A mixture of 10 g of 7-chloroheptanoic acid, 8.8 g of 7-aminoheptanoic acid, and 100 ml of 5% ammonia was heated at 100° for two hours. After the operations described above we obtained 3.7 g (22%) of 7,7'-iminodiheptanoic acid and 9.65 g of 7-aminoheptanoic acid.

2. Hydrochloride of Diethyl 7,7'-Iminodiheptanoate

The hydrochloride was prepared by passing dry hydrogen chloride into a suspension of 10 g of the imino acid in 50 ml of absolute ethanol for two hours at 60°. Removal of alcohol under reduced pressure and addition of ether gave 4.8 g (36%) of the hydrochloride, m.p. 148-150°, raised by recrystallization from benzene to 155-156°.

Found %: C 59.26; 59.01; H 10.02; 10.01; Cl 9.52; 9.32 $C_{18}H_{36}O_4NCl$. Calculated %: C 59.08; H 9.92; Cl 9.69.

3. Diethyl 7, 7'-Iminodiheptanoate

The diethyl ester was obtained in 67% yield by treating the hydrochloride with moist silver oxide; b.p. 177° (1 mm); $n^{20}D$ 1.4528; d^{20}_4 0.9626; found MR 92.46; calculated MR 92.23.

Found %: C 65.29; 65.30; H 10.68; 10.55 $C_{18}H_{35}O_4N$. Calculated %: C 65.61; H 10.70.

4. Monoethyl Ester of the Monoamide of 7,7'-Iminodiheptanoic Acid.

Long standing of the diethyl ester in admixture with ethanol saturated with ammonia gave the monoethyl ester of the monoamide of 7,7'-iminodiheptanoic acid; m.p. 83-84° (from benzene). A little of the diamide was isolated also.

Found %: N 8.92; 8.97 $C_{16}H_{32}O_3N_2$. Calculated %: N 9.32.

5. Hydrochloride of 7,7'-Iminobisheptanamide

The hydrochloride of the diamide was prepared in 80% yield from the hydrochloride of the diethyl ester as described in the previous experiment; m.p. 205° (from ethanol).

Found %: C 54.77; 54.88; H 9.83; 9.89 $C_{14}H_{30}O_2N_2Cl$. Calculated %: C 54.61; H 9.82.

6. 7,7'-(Acetylimino)diheptanoic Acid

7,7'-Iminodiheptanoic acid (16 g) was boiled with acetic anhydride (50 ml). After complete removal of excess of acetic anhydride and acetic acid and recrystallization of the residue from a mixture of acetone and ether, we obtained 13.6 g (73%) of the acetyl derivative, m.p. 67-69°, raised by further recrystallization from acetone-ether to 73-74°.

Found %: C 60.66; 60.52; H 9.25; 9.34; N 4.46; 3.96 $C_{16}H_{29}O_5N$. Calculated %: C 60.92; H 9.27; N 4.44.

7. Diethyl 7,7'-(Methylimino)diheptanoate

A solution of 40 g of ethyl 7-chloroheptanoate in 120 ml of dry benzene containing 10 g of methylamine was heated for three hours in an autoclave at 130° (in a bath). The benzene solution was washed with water and dried with sodium sulfate; benzene was distilled off. Vacuum distillation of the residue gave two fractions: one of b.p. 87-120° (2.5 mm), from which crystals were precipitated on standing, and another of b.p. 175-187° (2.5 mm). The crystals were filtered off and washed with ether (3.45 g); m.p. 75-80°. Vacuum distillation of the filtrate gave 15.9 g of unchanged ethyl 7-chloroheptanoate, b.p. 82-83° (2.5 mm) and $n^{20}D$ 1.4435, and 4.4 g of a high-boiling fraction, b.p. 180-183° (3 mm).

The high-boiling fractions were combined and again fractionated. We obtained 8.6 g (25%) of diethyl

7,7'-(methylimino)diheptanoate; b.p. 176-177° (2 mm); $n^{20}D$ 1.4520; d^{20}_4 0.9510; found MR 97.44; calculated MR 97.19.

Found %: C 66.43; 66.56; H 10.86; 10.80 $C_{19}H_{37}O_4N$. Calculated %: C 66.43; H 10.86.

Recrystallization of the crystals from a mixture of alcohol and ether gave 2.9 g of the hydrochloride of ethyl 7-methylaminoheptanoate, m.p. 108-109°.

Found %: C 53.46; 53.62; H 9.88; 10.03; N 6.35; 6.35 $C_{10}H_{22}O_2NCl$. Calculated %: C 53.87; H 9.95; N 6.29.

8. 7,7'-(Methylimino)diheptanoic Acid

This was prepared by the hydrolysis of 3 g of the diethyl ester with 6% hydrochloric acid. The hydrochloric acid was distilled off under reduced pressure, and 4.2 g of solid residue remained. A solution of 2.8 g of this substance in 30 ml of water was passed through Kationit SDV-3 [7]. The resin was washed free from chloride ion with water, and the imino acid was eluted with 5% ammonia solution. The eluate was evaporated to dryness, and the semisolid residue was washed with acetone. The product (1.3 g) was 7,7'-(methylimino)diheptanoic acid, m.p. 115-120°, raised to 134° by two recrystallizations from a mixture of water and acetone.

Found %: C 62.06; 61.95; H 9.94; 9.99; N 4.68; 4.81 $C_{15}H_{29}O_4N$. Calculated %: C 62.68; H 10.20; N 4.88.

9. Hydrochloride of the Monoethyl Ester of 7,7'-(Methylimino)diheptanoic Acid

The hydrochloride was obtained by long standing of the oil liberated when dry hydrogen chloride was passed into an ethereal solution of 1 g of diethyl 7,7'-(methylimino)diheptanoate. The precipitated crystals (0.92 g) were filtered off and washed with ether; m p. 78-82°, raised to 89-90° by two recrystallizations from a mixture of alcohol and ether.

Found %: C 57.93; 57.97; H 9.64; 9.53; N 4.08; 4.06 $C_{17}H_{34}O_4NCl$. Calculated %: C 58.01; H 9.73; N 3.98.

10. 9,9'-Iminodinonanoic Acid

Ammonolysis of 20 g of 9-chlorononanoic acid with 150 ml of 25% ammonia at 100° for 90 minutes gave an 18% yield of 9,9'-iminodinonanoic acid.

The isolation and purification of 9,9'-iminodinonanoic acid were carried out by the procedure described for the first experiment. The pure imino acid had m.p. 201-202°.

Found %: C 65.09; 65.21; H 10.47; 10.54 $C_{18}H_{35}O_4N$. Calculated %: C 65.61; H 10.70.

From the filtrate we isolated 11.9 g of 9-aminononanoic acid.

11. Hydrochloride of Diethyl 9.9'-Iminodinonanoate

The hydrochloride was prepared by the procedure described for Experiment 2; yield 84%; m.p. 155-156° (from alcohol-ether).

Found %: C 62.37; 62.32; H 10.46; 10.53; N 3.11; 3.28 $C_{22}H_{44}O_4NCl$. Calculated %: C 62.60; H 10.51; N 3.32.

12. 11,11'-Iminodiundecanoic Acid

This was prepared in 32% yield (calculated for crude product) by the ammonolysis of 15 g of 11-chloroundecanoic acid with 200 ml of concentrated ammonia. After complete removal of ammonia, the iminodiundecanoic acid was isolated from hot dilute solution. The imino acid was purified as in Experiment 1. Pure 11,11'-iminodiundecanoic acid had m.p. 190-191°.

Found %: C 68.30; 68.10; H 11.25; 11.22; N 3.65; 3.71 $C_{22}H_{43}O_4N$. Calculated %: C 68.52; H 11.24; N 3.63.

13. Hydrochloride of Diethyl 11,11'-Iminodiundecanoate

This was prepared in 46% yield by the procedure described for Experiment 2; m.p. 157° (from alcohol-ether).

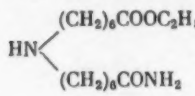
Found %: C 65.56; 65.62; H 10.91; 10.90; N 2.87; 2.80 $C_{26}H_{52}O_4NCl$. Calculated %: C 65.31; H 10.96; N 2.93.

SUMMARY

Starting from the corresponding ω-chloro carboxylic acids we prepared ω,ω'-imino dicarboxylic acids and their N- and O- derivatives; the products had the following structures:

$HN[(CH_2)_6COOH]_2$, $HN[(CH_2)_8COOH]_2$, $HN[(CH_2)_{10}COOH]_2$, $HCl\cdot NH[(CH_2)_6COOC_2H_5]_2$; $HCl\cdot NH[(CH_2)_8COOC_2H_5]_2$, $HCl\cdot NH[(CH_2)_{10}COOC_2H_5]_2$, $HN[(CH_2)_6COOC_2H_5]_2$, $CH_3N[(CH_2)_6COOC_2H_5]_2$, $CH_3N[(CH_2)_6COOH]_2$,

$CH_3C(=O)-N[(CH_2)_6COOH]_2$ $HCl\cdot NH[(CH_2)_6C(=O)-NH_2]_2$,



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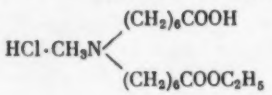

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AMINES CONTAINING THE CCl_3 GROUP AND THEIR BASIC DISSOCIATION CONSTANTS

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When present in a saturated carbon chain, the CCl_3 group exerts a powerful negative induction effect. This effect is manifested by the increase in strength produced in a carboxylic acid by the introduction of a CCl_3 group into the carbon chain of the acid; the effect is still appreciable even in 5,5,5-trichloropentanoic acid [1], in which the CCl_3 and COOH groups are separated by three methylene groups. The electron-accepting power of the CCl_3 group is manifested also in its orienting effect on the addition of unsymmetrical reagents to 3,3,3-trichloropropene $CH_2 = CH - CCl_3$. Thus, in the reaction with hypobromous acid, addition to 3,3,3-trichloropropene is in the opposite direction to addition to propene [2]; similar behavior is observed in "conjugated" chlorination in a sulfuric or acetic acid medium [3].

The object of the present investigation was to determine the effect of the CCl_3 group on the basic character of the amino group in compounds of the series $NH_2(CH_2)_nCCl_3$. The values obtained for the dissociation constants K_B are given in Table 1. For comparison purposes, we give also the dissociation constants of amines containing the $CH_2=CH$ group.

TABLE 1

Dissociation Constants K_B in Water at 20°

Formula of amine	K_B	Formula of amine	K_B
$CCl_3CH_2NH_2$	$2 \cdot 10^{-9}$	$CCl_3(CH_2)_4NH_2$	$9 \cdot 10^{-5}$
$CCl_3(CH_2)_2NH_2$	$3 \cdot 10^{-5}$	$CCl_2=CH-CH_2NH_2$	$2 \cdot 10^{-5}$
$CCl_3(CH_2)_3NH_2$	$6 \cdot 10^{-5}$	$CCl_2=CH-(CH_2)_2NH_2$	$7 \cdot 10^{-5}$

The dissociation constants of ethylamine, propylamine, and butylamine are $3.4 \cdot 10^{-4}$ (25°), $4.7 \cdot 10^{-4}$ (25°), and $4.1 \cdot 10^{-4}$ (25°), respectively; K_B for allylamine [4] is $5.7 \cdot 10^{-5}$ (20°). Hence, the replacement of methyl by trichloromethyl reduces the basic dissociation constant of an amine by a factor of 10^4 when the CCl_3 and NH_2 groups are separated by one methylene group, but only about tenfold when the two groups are separated by two or more methylene groups. Such a rapid fall in the effect is characteristic of an induction effect. When we compare the CCl_3 and $CCl_2=CH$ groups it is seen that the former has a considerably more powerful electron-accepting induction effect than the latter: for $CCl_3CH_2NH_2$, $K_B = 2 \cdot 10^{-9}$, whereas for $CCl_2=CHCH_2NH_2$ $K_B = 2 \cdot 10^{-5}$. Comparison of the dissociation constants of $CCl_2 = CHCH_2NH_2$ and $CCl_3CH_2CH_2NH_2$ shows that the double bond is a better conductor of the effect of the chlorine than the single bond; the two chlorine atoms of the first compound appear to reduce the basic character of the amine to a greater extent than the three chlorine atoms of the second. A reservation must be made, however; in making this statement we have neglected the effect of the double bond itself on the dissociation of the amine. As will be seen from the case of allylamine, the effect is to reduce the dissociation constant.

The amines were synthesized as follows: 3,3,3-Trichloropropylamine, 4,4,4-trichlorobutylamine, and 4,4-dichloro-3-butenylamine were prepared from the corresponding carboxylic acids by the action of hydrazoic acid in presence of concentrated sulfuric acid, e.g.

$$CCl_3CH_2CH_2COOH + HN_3 \xrightarrow{H_2SO_4} CCl_3CH_2CH_2NH_2.$$

The yields of amines were low because of the occurrence of dehydrochlorination and hydrolysis side reactions under the action of sulfuric acid. 5,5,5-Trichlorpentylamine was prepared by the action of alcoholic ammonia on 1,1,1,5-tetrachloropentane, as described previously [5]. 2,2,2-Trichloroethylamine was prepared as follows:

$$CH_2 = CCl_2 + ClNO_2 \rightarrow NO_2CH_2CCl_3 \xrightarrow{SnCl_2+HCl} NH_2CH_2CCl_3.$$

In the addition of nitryl chloride to vinylidene chloride, 1,1-dichloro-2-nitroethylene was obtained as well as 1,1,1-trichloro-2-nitroethane. 3,3-Dichloroallylamine was synthesized by the action of hexamethylenetetramine on 1,1,3-trichloropropene, with subsequent decomposition of the adduct with hydrochloric acid. In an attempt to prepare 3,3-dichloroallylamine by the action of alcoholic ammonia on 3,3,3-trichloropropene or 1,1,3-trichloropropene, we obtained only $(CCl_2{=}CH{-}CH_2)_2NH$ in low yield. Amines containing the CCl_3 group are liquids which can be vacuum-distilled without decomposition. 2,2,2-Trichloroethylamine has a strong odor of camphor. N-Benzoyl derivatives of amines in the series $NH_2(CH_2)_nCCl_3$ show a periodicity in melting points from the C_3 amine onward; the odd members of the series melt higher than the nearest even members (see Table 2).

TABLE 2

Melting Points in the Series $CCl_3(CH_2)_nNHCOC_6H_5$

Formula of amine	M.p. (°C)	Formula of amine	M.p. (°C)
$CCl_3CH_2NHCOC_6H_5$	132—133	$CCl_3(CH_2)_4NHCOC_6H_5$ [5]	95—96
$CCl_3(CH_2)_2NHCOC_6H_5$	115—116	$CCl_3(CH_2)_5NHCOC_6H_5$ [5]	70,5—71,5
$CCl_3(CH_2)_3NHCOC_6H_5$	75—76	$CCl_3(CH_2)_6NHCOC_6H_5$ [5]	91—92

EXPERIMENTAL

1). 3,3,3-Trichloropropylamine. Concentrated sulfuric acid (110 ml) was added over a period of one hour to a stirred solution of 41 g of 4,4,4-trichlorobutyric acid in 200 ml of benzene containing 13.4 g of hydrazoic acid at 40°. The mixture was stirred further at 40-50° until the evolution of nitrogen ceased (90 minutes). The cooled mixture was poured into ice water, the benzene layer was separated, and the sulfuric acid solution was rendered alkaline by addition of sodium hydroxide solution under strong cooling. The oil that separated was extracted with ether. The extract was dried over sodium sulfate, and ether was distilled off under slightly reduced pressure. The residue was distilled, and at 70-74° (13 mm) we collected 12.5 g of 3,3,3-trichloropropylamine, which apparently contained some 3,3-dichloroallylamine. For purification the mixture of amines was poured into concentrated hydrochloric acid, and the precipitated hydrochloride was filtered off and recrystallized from hydrochloric acid. 3,3,3-Trichloropropylamine hydrochloride melted at 232-233° (in a sealed capillary).

Found %: C 18.35; 18.18; H 3.60; 3.62; N 7.20; 7.02. $C_3H_7Cl_4N$. Calculated %: C 18.09; H 3.52; N 7.03.

By rendering a solution of the hydrochloride alkaline we isolated 3,3,3-trichloropropylamine; b.p. 73-73.5° (20 mm); $n^{20}D$ 1.4920; d^{20}_4 1.3809; found MR 34.14; calculated MR 34.08.

Found %: C 22.28; 22.32; H 3.71; 3.60. $C_3H_6Cl_3N$ Calculated %: C 22.15; H 3.69.

Its N-benzoyl derivative had m.p. 115-116° (from benzene).

Found %: N 5.00; 5.06. $C_{10}H_{10}Cl_3NO$. Calculated %: N 5.21.

2). 4,4,4-Trichlorobutylamine. Concentrated sulfuric acid (43 ml) was added to a stirred solution of 16.8 g of 5,5,5-trichlorovaleric acid in 120 ml of benzene containing 4.8 g of hydrazoic acid at 40-50°. The mixture was stirred further at 40-50° for three hours. Treatment of the reaction mixture as in the preceding experiment

gave 8.6 g of a mixture of amines of b.p. 88-91° (18 mm), from which we isolated the hydrochloride of 4,4,4-trichlorobutylamine, m.p. 213,214° (from concentrated hydrochloric acid or a mixture of alcohol and ether).

Found %: C 22.73; 22.62; H 4.36; 4.33; N 6.43; 6.42. $C_4H_9Cl_4N$. Calculated %: C 22.53; H 4.22; N 6.57.

From the hydrochloride we obtained 4,4,4-trichlorobutylamine; b.p. 50-51° (2 mm); $n^{20}D$ 1.4925; d^{20}_4 1.3140; found MR 49.11; calculated MR 49.01.

Found %: N 8.09; 8.07 . $C_4H_8Cl_3N$. Calculated %: N 7.93.

Its N-benzoyl derivative had m.p. 75-76° (from a mixture of benzene and petroleum ether).

Found %: N 4.76; 4.82. $C_{11}H_{22}Cl_3NO$. Calculated %: N 4.98.

3). 1,1,1-Trichloro-2-nitroethane. A mixture of 56 g of vinylidene chloride and 0.5 g of anhydrous ferric chloride was stirred at a temperature of from − 2° to 0° while the required amount of nitryl chloride was passed in. The mixture was stirred at 0° for three hours and was then left overnight. It was then poured into water, washed with dilute hydrochloric acid, and dried over calcium chloride. Fractionation through a column gave 6 g of 1,1-dichloro-2-nitroethylene and 18 g of 1,1,1-trichloro-2-nitroethane; b.p. 69-70° (9 mm); $n^{20}D$ 1.4857; d^{20}_4 1.6129; found MR 31.66; calculated MR 31.76.

Found %: C 13.20; 13.26; H 1.11; 1.05; Cl 59.67; 59.51. $C_2H_2Cl_3NO_2$. Calculated %: C 13.44; H 1.12; Cl 59.69.

1,1-Dichloro-2-nitroethylene had b.p. 52-53° (9 mm); $n^{20}D$ 1.5101; d^{20}_4 1.5797.

Found %: C 16.91; 17.01; H 0.85; 0.87 $C_2HCl_2NO_2$. Calculated %: C 16.90; H 0.70.

4). 2,2,2-Trichloroethylamine. 1,1,1-Trichloro-2-nitroethane (16 g) was added gradually to a stirred solution of 75 g of $SnCl_2 \cdot 2H_2O$ in 120 ml of concentrated hydrochloric acid. The reaction was highly exothermic: the temperature rose to 100°, and it was necessary to apply cooling. The 1,1,1-trichloro-2-nitroethane dissolved completely. The solution was stirred at 90° for 30 minutes and then cooled; the crystalline precipitate was filtered off. The filtrate was evaporated down under reduced pressure, the residue was dissolved in water, and the resulting solution was treated with sodium hydroxide solution under cooling. The amine was extracted with ether. When treated with sodium hydroxide solution, the crystalline precipitate also gave an amine. The ether extracts were dried over sodium sulfate. Vacuum distillation gave 5.2 g of 2,2,2-trichloroethylamine; b.p. 43-44° (20 mm); $n^{20}D$ 1.4915, d^{20}_4 1.4507; found MR 29.67; calculated MR 29.46.

Found %: C 16.23; 16.18; H 2.94; 2.86. $C_2H_4Cl_3N$. Calculated %: C 16.16; H 2.70.

2,2,2-Trichloroethylamine hydrochloride did not melt below 250°, but it sublimed.

Found %: N 7.70; 7.55. $C_2H_5Cl_4N$. Calculated %: N 7.56.

The oxalate had m.p. 169-180° (from alcohol).

Found %: N 7.32; 7.32. $C_6H_{10}Cl_6N_2O_4$. Calculated %: N 7.23.

The N-benzoyl derivative had m.p. 132-133° (from benzene).

Found %: N 5.46; 5.52. $C_9H_8Cl_3NO$. Calculated %: N 5.54.

5). 3,3-Dichloroallylamine. 1,1,3-Trichloropropene (32 g) was added to a heated solution of 31.5 g of hexamethylenetetramine and 37 g of sodium iodide, and the mixture was left overnight. A copious precipitate formed. The mixture was then saturated with dry hydrogen chloride, and alcohol was distilled off from a water bath; the residue was dissolved in water, and the solution was rendered alkaline with sodium hydroxide solution under cooling. The amine was extracted with ether, and the ether extract was dried over sodium sulfate. The product, amounting to 14.3 g, was 3,3-dichloroallylamine; b.p. 47-48° (12 mm); $n^{20}D$ 1.5010; d^{20}_4 1.2919; found MR 28.73; calculated MR 28.74.

Found %: N 10.98; 11.02. $C_3H_5Cl_2N$. Calculated %: N 11.11.

The hydrochloride had m.p. 249-250° (from hydrochloric acid).

Found %: C 21.99; 22.08; H 3.31; 3.54; N 8.73; 8.77 $C_3H_6Cl_3N$. Calculated %: C 22.15; H 3.69; N 8.61.

Heating of a solution of 30 g of 1,1,3-trichloropropene in 100 ml of alcohol containing 10.5 g of ammonia for three hours at 100° in an autoclave gave about 5 g of an amine, b.p. 80-140° (3 mm), and from this we prepared 3,3,3',3'-tetrachlorodiallylamine hydrochloride, m.p. 205-206° (from hydrochloric acid).

Found %: N 4.94; 4.98 $C_6H_8Cl_5N$. Calculated %: N 5.15.

6). 4,4-Dichloro-3-butenylamine. Concentrated sulfuric acid (70 ml) was added over a period of one hour to a solution of 20.4 g of 5,5-dichloro-4-pentenoic acid in 130 ml of benzene containing 9 g of hydrazoic acid at 37-38°. The reaction mixture was stirred for three hours at 40-45° and then treated as in the preparation of 3,3,3-trichloropropylamine. This gave 5.2 g of 4,4-dichloro-3-butenylamine; b.p. 79-80° (20 mm); $n^{20}D$ 1.4938; d^{20}_4 1.2210, found MR 33.40; calculated MR 33.36.

Found %: C 34.15; 31.10; H 5.12; 5.08 $C_4H_7Cl_2N$. Calculated %: C 34.28; H 5.00.

Its hydrochloride had m.p. 186-187° (from a mixture of alcohol and ether).

Found %: C 27.18; 27.39; H 4.57; 4.43; N 7.77; 7.79. $C_4H_8Cl_3N$. Calculated %: C 27.23; H 4.54; N 7.94.

The dissociation constants of the amines were determined from the results of pH measurements on $5 \cdot 10^{-3}$ M aqueous solutions of their hydrochlorides carried out with an LP-5 potentiometer.

SUMMARY

Dissociation constants were measured for amines of the series $CCl_3(CH_2)_nNH_2$, in which n = 1-4, and for amines of the series $CCl_2{=}CH(CH_2)_nNH_2$, in which n = 1 and 2.

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ACTION OF ORGANOMAGNESIUM COMPOUNDS ON 3-ALKOXY-1-CHLORO-1-ALKYNES

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Substituted haloacetylenes ($RC{\equiv}C{-}X$, in which X is halogen) vary in their behavior toward organomagnesium compounds in a way which depends on the structure of the radical, the identity of the halogen, and the absence or presence of a catalyst of the cobalt chloride type during the reaction. In absence of such catalysts, substituted bromo- and iodo-acetylenes react with oranomagnesium compounds as follows [1,2]:

$$RC{\equiv}C-Br\ (I) + R'MgX \rightarrow RC{\equiv}C-MgX + R'Br\ (I)$$

In presence of cobalt chloride or cuprous chloride, this exchange reaction is accompanied in some measure by replacement of halogen with formation of disubstituted acetylenes [1,2]:

$$RC{\equiv}C-Br + R'MgX \xrightarrow{CoCl_2} RC{\equiv}C-R'.$$

The action of organomagnesium compounds on substituted chloroacetylenes in presence of catalysts has not been studied. In absence of catalysts chloroacetylenes ($RC{\equiv}C-Cl$, in which R is alkyl or aryl) do not react with organomagnesium compounds [3], but under these conditions dichloroacetylene reacts with formation of substituted chloroacetylenes [3]:

$$Cl-C{\equiv}C-Cl + RMgX \rightarrow RC{\equiv}C-Cl.$$

We showed recently [4] that, in absence of catalysts, acetals of chloropropiolaldehyde give acetals of acetylenic aldehydes with organomagnesium compounds:

$$Cl-C{\equiv}C-CH(OR')_2 + RMgX \rightarrow RC{\equiv}C-CH(OR)_2.$$

The present paper concerns the reaction of organomagnesium compounds with 3-alkoxy-1-chloro-1-alkynes, which in absence of catalysts leads to disubstituted acetylenes:

$$RCH(OAlk)-C{\equiv}C-Cl + R'MgX \rightarrow RCH(OAlk)-C{\equiv}CR'.$$

Reaction in this way is accompanied to some extent by an exchange reaction with formation of $RCH(OAlk)C{\equiv}C-MgX$. We studied the reactions of $n\text{-}C_4H_9CH(OC_2H_5)C{\equiv}C-Cl$, $n\text{-}C_4H_9CH(OC_4H_9)C{\equiv}C-Cl$, and $C_2H_5CH(OC_4H_9)C{\equiv}CCl$ with $n\text{-}C_4H_9MgBr$, C_2H_5MgBr, $i\text{-}C_4H_9MgBr$, $i\text{-}C_3H_7MgBr$ and C_6H_5MgBr. In the reaction of phenylmagnesium bromide with $n\text{-}C_4H_9CH(OC_4H_9)C{\equiv}C-Cl$ and with $C_2H_5CH(OC_4H_9)-C{\equiv}C-Cl$, apart from the corresponding phenylacetylenes, biphenyl was formed in appreciable amount. In almost all cases the reactions of these chloroacetylenes with organomagnesium compounds proceeded with evolution of heat. Unlike these chloroacetylenes, 1-chloro-1-hexyne and 1,5-dichloro-1-pentyne did not react with butylmagnesium bromide in absence of catalysts, which is in accord with previous results [3]. In presence of cobalt chloride butylmagnesium bromide reacted vigorously with 1-chloro-1-hexyne, but no $C_4H_9C{\equiv}CC_4H_9$ was found in the reaction product, which consisted of a mixture of higher-boiling compounds containing halogen and oxygen. Unlike the chloro compounds, 1-bromo-3-butoxy-1-heptyne reacted with butylmagnesium bromide only by the exchange reaction of the type indicated above for other substituted bromoacetylenes.

When we examine the now known types of chloroacetylenes which exchange chlorine for alkyl or aryl in their reactions with organomagnesium compounds, we can see a formal resemblance between such chloroacetylenes and other chloro compounds that can exchange their chlorine for an organic group under the action of organomagnesium compounds. Thus, with organomagnesium compounds RMgX, Cl_2, $ClCH(OAlk)_2$, and $R'CH(OAlk)Cl$ should give RCl, $RCH(OAlk)_2$, and $R'CH(OAlk)R$, respectively. If in Cl_2, $ClCH(OAlk)_2$, and $R'CH(OAlk)Cl$ we

interpose a $-C \equiv C-$ grouping between the chlorine atom and the rest of the molecule, then we obtain $ClC \equiv CCl$, $ClC \equiv CCH(OAlk)_2$, and $ClC \equiv CCH(OAlk)R'$, which are also able to undergo a similar reaction with organomagnesium compounds. On the other hand, alkyl chlorides RCH_2Cl do not usually react with organomagnesium compounds; similarly, $RCH_2C \equiv CCl$ also does not react with organomagnesium compounds. Hence, in relation to this reaction we may use the term "ethynylogy" in a sense analogous to that of "vinylogy".

3-Alkoxy-1-chloro-1-alkynes were prepared as follows:

$$CCl_2=CH-\underset{\diagdown\,OAlk}{\overset{\diagup\,Cl}{CH}}+RMgX \rightarrow CCl_2=CH-CH(OAlk)R \xrightarrow{KOH} ClC \equiv C-CH(OAlk)R.$$

The presence of a triple bond in the products was confirmed by the infrared spectrum. 1-Chloro-3-ethoxy-1-heptyne has an intense absorption band at 2230 cm^{-1} (for disubstituted acetylenes [5] the absorption band lies within the range 2190-2260 cm^{-1}). In the hydration of 1-chloro-3-ethoxy-1-heptyne in presence of mercury sulfate in aqueous-methanolic solution we did not succeed in isolating the corresponding ketone in a pure state, but treatment of the reaction products with 2,4-dinitrophenylhydrazine gave an orange "dinitrophenylhydrazone", m.p. 195-196° (from glacial acetic acid). Analysis showed that this hydrazone contained two 2,4-dinitrophenylhydrazine residues and did not contain chlorine. When treated with ethanol it was converted into a dark-red dinitrophenylhydrazone of m.p. 196-197° (from alcohol), and analysis showed that this contained only one 2,4-dinitrophenylhydrazine residue. These hydrazones were not investigated more closely. The presence of a triple bond in the products ($RCH(OAlk)C \equiv CR'$) was confirmed by the infrared spectrum. 7-Butoxy-5-undecyne had a strong absorption band at 2260 cm^{-1}.

1-Bromo-3-butoxy-1-heptyne was synthesized from 3-butoxy-1-heptyne, which was treated with potassium hypobromite in an alkaline medium [6]. 1,5-Dichloro-1-pentyne was prepared by the action of sodium acetylide in liquid ammonia on 1,1,5-trichloro-1-pentene:

$$Cl(CH_2)_3CH=CCl_2+HC \equiv CNa \rightarrow Cl(CH_2)_3C \equiv CCl.$$

The preparation of 1,5-dichloro-1-pentyne from 1,1,5-trichloro-1-pentene by the action of sodamide in liquid ammonia gave a lower yield.

EXPERIMENTAL

3-Butoxy-1,1-dichloro-1-heptene. 3-Butoxy-1,1,3-trichloropropene (108 g) was added slowly to a cooled stirred ethereal solution of butylmagnesium bromide, which was taken in 20% excess. The reaction mixture was heated for 30 minutes, cooled, and poured into a solution of ammonium chloride. The ethereal solution was dried over potassium carbonate. The product (102 g) was 3-butoxy-1,1-dichloro-1-heptene; b.p. 122-124° (14 mm); $n^{20}D$ 1.4555 d^{20}_4 1.0130; found MR 63.91; calculated MR 64.01.

Found %: C 55.12; 55.02; H 8.32; 8.26 $C_{11}H_{20}Cl_2O$. Calculated % C 55.23; H 8.40.

Similarly, from 107 g of 3-butoxy-1,1,3-trichloropropene and ethylmagnesium bromide we obtained 92 g of 3-butoxy-1,1-dichloro-1-pentene; b.p. 83-85° (10 mm); $n^{20}D$ 1.4523; d^{20}_4 1.0387; found MR 54.81; calculated MR 54.68.

Found %: C 50.98; 51.13; H 7.40; 7.45 $C_9H_{16}Cl_2O$. Calculated %: C 51.18; H 7.58.

1-Chloro-3-ethoxy-1-heptyne. A solution of 63 g of 1,1-dichloro-3-ethoxy-1-heptene and 23 g of potassium hydroxide in 100 ml of ethanol was heated at 140-150° for five hours in an autoclave. The reaction mixture was poured into water, and the product was extracted with ether. The extract was dried over potassium carbonate. Fractionation through a column gave 29.3 g of 1-chloro-3-ethoxy-1-heptyne; b.p. 60.5-61° (7 mm); $n^{20}D$ 1.4411, d^{20}_4 0.9515; found MR 48.44; calculated MR 48.27.

Found %: C 61.58; 61.62; H 8.35; 8.41 $C_9H_{15}ClO$. Calculated %: C 61.89; H 8.59.

Acidification of the aqueous-alcoholic solution resulted in the separation of 3.5 g of an oil, probably

3-ethoxyheptanoic acid; b.p. 126-128° (3 mm); $n^{20}D$ 1.4332; d^{20}_4 0.9556.

Found %: C 61.87; 61.95; H 10.23; 10.25 $C_9H_{18}O_3$. Calculated %: C 62.06; H 10.34.

3-Butoxy-1-chloro-1-heptyne. A solution of 140 g of 3-butoxy-1,1-dichloro-1-heptene and 46 g of potassium hydroxide in 400 ml of butyl alcohol was boiled for 6.5 hours. The mixture was cooled, and water was added to dissolve the potassium chloride; the alcoholic solution was separated from the aqueous layer and dried over potassium carbonate. Butyl alcohol was removed under reduced pressure, and the residue was distilled through a column. We obtained 72 g of 3-butoxy-1-chloro-1-heptyne; b.p. 98.5-99.5° (8 mm); $n^{20}D$ 1.4429; d^{20}_4 0.9326.

Found %: C 64.93; 64.98; H 9.50; 9.40 $C_{11}H_{19}OCl$. Calculated %: C 65.18; H 9.38.

3-Butoxy-1-chloro-1-pentyne. Boiling of a solution of 92 g of 3-butoxy-1,1-dichloro-1-pentene and 40 g of potassium hydroxide in 300 ml of butyl alcohol gave 18.2 g of 3-butoxy-1-chloro-1-pentyne; b.p. 67.5-68.5° (9 mm); $n^{20}D$ 1.4402; d^{20}_4 0.9507; found MR 48.40; calculated % MR 48.27.

Found %: C 61.82; 61.67; H 8.39; 8.44 $C_9H_{15}ClO$. Calculated %: C 61.89; H 8.59.

Reaction of 3-Butoxy-1-chloro-1-heptyne with Butylmagnesium Bromide. 3-Butoxy-1-chloro-1-heptyne (39 g) was added to butylmagnesium bromide (from 40 g of butyl bromide and 7.2 g of magnesium) in 100 ml of ether at such a rate as to maintain the ether at the boil by the heat of reaction. A precipitate of magnesium salts formed. After being heated for one hour, the reaction mixture was cooled and poured into a cold solution of ammonium chloride. The ethereal solution was washed with dilute hydrochloric acid and dried over potassium carbonate. Vacuum fractionation gave 3.5 g of 3-butoxy-1-heptyne (b.p. 86-85°)(14 mm); $n^{20}D$ 1,4270; d^{20}_4 0.8203) and 26.1 g of 7-butoxy-5-undecyne; b.p. 125-126° (8 mm); $n^{20}D$ 1.4412; d^{20}_4 0.8286; found MR 71.42; calculated MR 71.11.

Found %: C 80.05; 80.03; H 12.44; 12.47 $C_{15}H_{28}O$. Calculated %: C 80.35; H 12.50.

Reaction of 3-Butoxy-1-chloro-1-pentyne with Phenylmagnesium Bromide. 3-Butoxy-1-chloro-1-pentyne (17 g) was added gradually to phenylmagnesium bromide (from 25 g of bromobenzene and 3.7 g of magnesium) in 50 ml of ether. Reaction went with evolution of heat. The reaction mixture was heated for one hour and then treated as in the preceding experiment. We obtained 3.4 g of biphenyl and 11.5 g of 3-butoxy-1-phenyl-1-pentyne; b.p. 104-106° (2 mm); $n^{20}D$ 1.5125, d^{20}_4 0.9256.

Found %: C 83.07; 83.02; H 9.21; 9.18 $C_{15}H_{20}O$. Calculated %: C 83.33; H 9.26.

In the oxidation of 3-butoxy-1-phenyl-1-pentyne with potassium permanganate in alkaline solution we isolated benzoic acid, m.p. 122°. In the reaction of 10 g of 3-butoxy-1-chloro-1-heptyne with phenylmagnesium bromide we obtained 2.3 g of biphenyl and 4.7 g of 3-butoxy-1-phenyl-1-heptyne; b.p. 125-127° (2 mm); $n^{20}D$ 1.5072; d^{20}_4 0.9184.

Found %: C 83.10; 83.14; H 9.70; 9.71 $C_{17}H_{24}O$. Calculated %: C 83.60; H 9.86.

The results of reactions with other organomagnesium compounds are summarized in the table.

TABLE

Reaction product	Yield (%)	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	Found (%)		Calculated (%)	
					C	H	C	H
$C_4H_9CH(OC_2H_5)C\equiv C-C_2H_5$	74	80—81 (12)	1,4343	0,8282	78,13; 78,11	11,93; 11,96	78,57	11,90
$C_4H_9CH(OC_4H_9)C\equiv C-C_4H_9$-i	69	122—123 (8)	1,4402	0,8303	80,10; 80,02	12,27; 12,38	80,35	12,50
$C_4H_9CH(OC_4H_9)C\equiv C-C_3H_7$-i	43	105—10. (1)	1,4368	0,8373	79,58; 79,45	12,15; 12,19	80,00	12,38

1,5-Dichloro-1-pentyne. Sodium acetylide (from 8 g of sodium) in 400 ml of liquid ammonia was stirred at - 40° while 50 g of 1,1,5-trichloro-1-pentene was added. The mixture was stirred for three hours and then

left overnight. On the next day ether and water were added. The ethereal solution was washed with water and with dilute hydrochloric acid, and was filtered free of resinous products. It was dried over potassium carbonate, and ether was distilled off from the water bath. Vacuum distillation of the residue gave 23.1 g of 1,5-dichloro-1-pentyne; b.p. 47-28° (8 mm); $n^{20}D$ 1.4740; d^{20}_4 1.1662; found MR 33.02; calculated MR 33.02.

Found %: C 43.99; 44.15; H 4.48; 4.71 $C_5H_6Cl_2$. Calculated %: C 43.80; H 4.38.

By addition of methanol to 1,5-dichloro-1-pentyne in presence of a catalyst (HgO + $(C_2H_5)_2O \cdot BF_3$) we obtained 1,5-dichloro-1,1-dimethoxypentane; b.p. 100-101°(8 mm); $n^{20}D$ 1.4595.

Found %: C 41.62; 41.68; H 6.90; 7.08 $C_7H_{14}Cl_2O_2$. Calculated %: C 41.79; H 6.96.

The 2,4-dinitrophenylhydrazone of 1,5-dichloro-2-pentanone had m.p. 101-102° (from acetic acid).

Found %: N 16.64; 16.53 $C_{11}H_{12}Cl_2N_4O_4$. Calculated %: N 16.79.

Action of Butylmagnesium Bromide on 1-Chloro-1-hexyne. a) In absence of catalysts. 1-Chloro-1-hexyne (12 g) was added to butylmagnesium bromide (from 18 g of butyl bromide and 3.3 g of magnesium) in 40 ml of ether. No reaction appeared to occur. The solution was heated for 12 hours. After decomposition with ammonium chloride solution the ethereal layer was separated and dried over potassium carbonate. Distillation gave 8.2 g of unchanged 1-chloro-1-hexyne (b.p. 118-119°; $n^{20}D$ 1.4372) and about 1.2 g of a fraction boiling at 140-180° (8 mm), which contained halogen. Similarly, when an ethereal solution of butylmagnesium bromide was heated with 1,5-dichloro-1-pentyne for 15 hours, the latter was recovered unchanged in 90% yield.

b) In presence of cobalt chloride. 1-Chloro-1-hexyne (29 g) was added gradually to butylmagnesium bromide (from 45 g of butyl bromide and 8.3 g of magnesium) and cobalt chloride (0.5 g). Reaction was very vigorous. A large amount of magnesium salts was precipitated. The mixture was heated for 30 minutes, cooled, and poured into ammonium chloride solution. The ethereal solution was dried over potassium carbonate, and ether was distilled off. Vacuum distillation of the residue gave about 2 g of unchanged 1-chloro-1-hexyne and 26 g of a mixture boiling at 85-155° (8 mm). In the distillation of this mixture at atmospheric pressure it began to boil at 190° (the b.p. of dibutylacetylene (5-decyne) is 175°). Fractionation through a column gave a small fraction of b.p. 96-97° (8 mm) ($n^{20}D$ 1.4589; d^{20}_4 1.0446); it contained 31.8% of halogen and 8.5% of oxygen.

1-Bromo-3-butoxy-1-heptyne. As already described [7], 57 g of 3-butoxy-1,1-dichloro-1-heptene was added gradually to 22 g of finely granulated sodium in 220 ml of dry ether. We obtained 16.1 g of 3-butoxy-1-heptyne; b.p. 85-86° (14 mm); $n^{20}D$ 1.4275; d^{20}_4 0.8214; found MR 52.57; calculated MR 52.64.

Found %: C 78.60; 77.50; H 11.81; 11.93 $C_{11}H_{20}O$. Calculated % C 78.57; H 11.90.

3-Butoxy-1-heptyne (15 g) was stirred with a solution of 22 g of bromine and 35 g of potassium hydroxide in 200 ml of water at room temperature for 12 hours; the mixture was then extracted with chloroform. The chloroform solution was washed with water and dried over potassium carbonate. Vacuum distillation gave 12.9 g of 1-bromo-3-butoxy-1-heptyne; b.p. 118-120° (14 mm); $n^{20}D$ 1.4630; d^{20}_4 1.1306; found MR 60.17; calculated MR 60.34.

Found %: C 53.56; 53.55; H 7.52, 7.47 $C_{11}H_{19}BrO$. Calculated %: C 53.44; H 7.69.

Action of Butylmagnesium Bromide on 1-Bromo-3-butoxy-1-heptyne. 1-Bromo-3-butoxy-1-heptyne (6.5 g) was added dropwise to butylmagnesium bromide (from 7 g of butyl bromide) in 20 ml of ether. An exothermic reaction set in. The reaction mixture was decomposed with water, and as reaction products we obtained butyl bromide and 3-butoxy-1-heptyne; b.p. 84-85° (13 mm); $n^{20}D$ 1.4270.

SUMMARY

1. It was shown that substituted chloroacetylenes of structure $RCH(OAlk)-C \equiv C-Cl$ react with organomagnesium compounds with formation of disubstituted acetylenes $RCH(OAlk)-C \equiv C-R'$. Reaction of organomagnesium compounds with substituted bromoacetylenes of analogous structure results only in the exchange of bromine for MgX.

2. Substituted chloroacetylenes of structure $RCH_2C \equiv C-Cl$ do not react with organomagnesium

compounds. In presence of cobalt chloride, however, a reaction occurs, but no disubstituted acetylenes $RCH_2C \equiv C - R'$ are obtained: a mixture of products containing halogen and oxygen is formed.

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ADDITION OF SULFUR CHLORIDES TO RCH = CCl_2 IN NEUTRAL AND ACID MEDIA

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The reaction of sulfur chlorides (SCl_2 and S_2Cl_2) with halo olefins has been investigated only in the case of chloro- and fluoro-ethylenes. Pope and Smith [1] state that trichloroethylene does not react with S_2Cl_2 even after prolonged boiling, and at 140-150° in a sealed tube sulfur is liberated and the main product is pentachloroethane. According to a German patent [2], SCl_2 adds smoothly to vinyl chloride, vinylidene chloride, and trichloroethylene in presence of a Friedel-Crafts catalyst with formation of the corresponding sulfides, e.g. $CH_2 = CHCl + SCl_2 \longrightarrow S(CH_2CHCl_2)_2$. The addition of S_2Cl_2 to tetrachloroethylene [3,4] proceeds only at 100-125° and gives a mixture of products, the main one being $(ClF_2CCF_2)_2S_2$, which is accompanied by the corresponding mono- and tri-sulfides and by ClF_2CCF_2SCl and ClF_2CCF_2SSCl. The reaction of tetrafluorethylene with SCl_2 gives similar results. Knuniants and Bykhovskaia [5] studied the reaction of SCl_2 and S_2Cl_2 with vinylidene fluoride. In the case of SCl_2 the main product was $(ClF_2CCH_2)_2S_2$, but the yield was only 15-20%. Vinylidene fluoride reacted with S_2Cl_2 at 100° and gave mainly $(ClF_2CCH_2)_2S_2$; it gave also the corresponding polysulfides, of which the trisulfide was isolated.

We have investigated the addition of sulfur chlorides, mainly S_2Cl_2, to compounds containing the $CCl_2 = CH$ group, in a neutral medium and in a medium of concentrated sulfuric acid. It was found that S_2Cl_2 adds readily to 1,1-dichloropropene, 1,1,3-trichloropropene, and 1,1,5-trichloro-1-pentene in carbon tetrachloride solution at 35-45° in presence of a little anhydrous ferric chloride. The reaction is exothermic. In absence of ferric chloride no appreciable addition occurs at the boiling point of carbon tetrachloride:

$$RCH = CCl_2 + S_2Cl_2 \xrightarrow{FeCl_3} (RCHCCl_3)_2 \quad (S\text{ on the CH})$$

We studied the reaction of SCl_2 with the 2,2-dichlorovinyl group for the case of 1,1,3-trichloropropene, and we obtained a disulfide and pentachloropropane:

$$3ClCH_2CH = CCl_2 + 2SCl_2 \xrightarrow{FeCl_3} (ClCH_2CHCCl_3)_2 + ClCH_2CHClCCl_3 \quad (S\text{ on the CH})$$

The formation of the corresponding monosulfide was not observed. The fact that the two disulfides obtained in the reaction of 1,1,3-trichloropropene with SCl_2 and with S_2Cl_2 were identical was proved by the absence of melting point depression in a mixture test. Bis[4-chloro-1-(trichloromethyl)butyl] disulfide, which was obtained from 1,1,5-trichloro-1-pentene, could not be vacuum-distilled without decomposition. Reduction of this disulfide with amalgamated aluminum in moist ether gave 1,1,1,5-tetrachloro-2-pentanethiol in low yield:

$$\left[Cl(CH_2)_3CHCCl_3 \text{ (S on the CH)}\right]_2 \xrightarrow[Al\,|\,Hg]{H_2} Cl(CH_2)_3CHCCl_3 \quad (SH\text{ on the CH})$$

In addition to the thiol we obtained some 1,1,5-trichloro-1-pentene, probably as a result of the simultaneous elimination of neighboring sulfur and chlorine atoms during the reduction. The formation of the tetrachloropentanethiol from the disulfide proves the structure of the latter and therefore also the direction in which S_2Cl_2 adds to $RCH = CCl_2$, because addition in the opposite direction would give the grouping CCl_2SH in the reduction product, which would then be unstable.

Reaction of S_2Cl_2 with the dichlorovinyl derivatives at 10-20° in presence of concentrated sulfuric acid resulted in the formation of α,α'-dithio dicarboxylic acids and proceeded as a "conjugated reaction":

$$2RCH=CCl_2 + S_2Cl_2 + H_2SO_4 \rightarrow (RCHCCl_2SO_3H)_2 \xrightarrow{H_2O} (RCH(S-)-COOH)_2.$$

This reaction does not proceed through the intermediate formation of $(R-CH(S-)-CCl_3)_2$ and subsequent hydrolysis of the CCl_3 group to carboxyl under the action of concentrated sulfuric acid, for under the reaction conditions used these disulfides are not hydrolyzed by concentrated sulfuric acid. Apart from this "conjugated-addition" reaction, hydrolysis of $RCH = CCl_2$ to the corresponding carboxylic acid proceeds to a slight extent. The dithio dicarboxylic acids obtained appeared to be contaminated also with polysulfides and could not therefore be prepared in the pure state; to isolate them in the pure state the acids were either converted into their dimethyl esters, which were vacuum-distilled, or reduced to the corresponding α-mercapto acids. Thus, 1,1-dichloro-1-butene gave 2,2'-dithiodibutyric acid, which was isolated as its dimethyl ester:

$$CH_3CH_2CH=CCl_2 + S_2Cl_2 \xrightarrow[H_2O]{H_2SO_4} (CH_3CH_2CH(S-)COOH)_2 \xrightarrow[H^+]{CH_3OH} (CH_3CH_2CH(S-)COOCH_3)_2.$$

1,1,5-Trichloro-1-pentene gave 2,2'-dithiobis [5-chlorovaleric acid], which was isolated as its dimethyl ester. Reduction of this ester with amalgamated aluminum in moist ether gave methyl 5-chloro-2-mercaptovalerate. This mercapto ester was dissolved in aqueous caustic alkali and there was appreciable evolution of heat; acidification of the solution gave tetrahydro-2-thiophenecarboxylic acid. Reduction of 2,2'-dithiobis [5-chlorovaleric acid] with zinc and hydrochloric acid in acetic acid solution gave 5-chloro-2-mercaptovaleric acid, and this, when vacuum-distilled or simply heated, lost hydrogen chloride and was converted into tetrahydro-2-thiophenecarboxylic acid:

$$Cl(CH_2)_3CH=CCl_2 + S_2Cl_2 \xrightarrow[H_2O]{H_2SO_4} \left[Cl(CH_2)_3CH(S-)COOH\right]_2 \xrightarrow{Zn+HCl}$$

$$\rightarrow Cl(CH_2)_3CH(SH)COOH \xrightarrow{-HCl} \begin{matrix} CH_2-CH_2 \\ | \quad | \\ CH_2 \quad CH-COOH \\ \quad \backslash S / \end{matrix}$$

For the purposes of identification, tetrahydro-2-thiophenecarboxylic acid was synthesized from sodium 2,5-dichlorovalerate and sodium sulfide in aqueous solution. From 1,1,7-trichloro-1-heptene and S_2Cl_2 in concentrated sulfuric acid we obtained the corresponding dithio dicarboxylic acid, which gave 7-chloro-2-mercaptoheptanoic acid on reduction.

EXPERIMENTAL

Bis[2,2,2-trichloro-1-(chloromethyl)ethyl] Disulfide. A mixture of 30 g of 1,1,3-trichloropropene, 20 ml of dry carbon tetarchloride, and 0.8 g of anhydrous ferric chloride was stirred at 40-45° while 13 g of S_2Cl_2 was added dropwise. The solution was heated for several minutes at 60-65°, cooled, and washed with dilute hydrochloric acid. It was then dried over calcium chloride, and solvent was removed under reduced pressure. After a time the residue crystallized; the product (33.2 g) was bis[2,2,2-trichloro-1-(chloromethyl)ethyl]disulfide, which, after recrystallization from alcohol, melted at 92-93° and boiled at 170-172° (2 mm).

Found %: C 17.07; 17.18; H 1.38; 1.40; S 15.26; 15.15 $C_6H_6Cl_8S_2$. Calculated %: C 16.90; H 1.40; S 15.02.

Reaction of 1,1,3-Trichloropropene with SCl_2. To a mixture of 30 g of 1,1,3-trichloropropene, 30 ml of carbon tetrachloride, and 0.8 g of ferric chloride at 45-50°, 12 g of SCl_2 was added dropwise. The solution was heated for 30 minutes at 65-70°, cooled, washed with dilute hydrochloric acid, and dried over calcium chloride. After removal of solvent the residue was vacuum-distilled. The products were 1,1,1,2,3-pentachloropropane (10.1 g; b.p. 47-48° (3 mm); $n^{20}D$ 1.5100; d^{20}_4 1.6104), the literature [6] gives b.p. 64-65° (8 mm); $n^{20}D$ 1.5105; d^{20}_4 1.6117) and bis[2,2,2-trichloro-1-(chloromethyl)ethyl] disulfide (18.6 g; b.p. 169-171° (2 mm); m.p. 92-93°). A mixture of this disulfide with that obtained in the reaction of S_2Cl_2 with 1,1,3-trichloropropene melted without depression at 92-93°.

Bis(2,2,2-trichloro-1-methylethyl) Disulfide. Reaction between 24 g of 1,1-dichloropropene and 13.5 g of S_2Cl_2 in presence of 1 g of ferric chloride gave 32.8 g of bis(2,2,2-trichloro-1-methylethyl) disulfide; b.p. 137.5-139° (2 mm); $n^{20}D$ 1.5769; d^{20}_4 1.5685; found MR 75.12; calculated MR 75.11.

Found %: C 20.41; 20.45; H 2.36; 2.40 $C_6H_8Cl_6S_2$. Calculated %: C 20.17; H 2.24.

1,1,1,5-Tetrachloro-2-pentanethiol. We prepared 43.6 g of undistilled bis [4-chloro-1-(trichloromethyl) butyl] disulfide by the procedure of the first experiment from 13.5 g of S_2Cl_2 in presence of 0.8 g of anhydrous ferric chloride, and 20 g of the product was reduced with amalgamated aluminum in moist ether. At first reduction proceeded with boiling of the ether, and hydrogen sulfide was evolved. After two hours the ether solution was filtered, washed with dilute hydrochloric acid, and dried over sodium sulfate. Vacuum distillation gave 5.7 g of 1,1,5-trichloro-1-pentene, b.p. 69-70° (8 mm) $n^{20}D$ 1.4892 and 4.1 g of 1,1,1,5-tetrachloro-2-pentanethiol; b.p. 119-120° (8 mm); $n^{20}D$ 1.5355; d^{20}_4 1.4390; found MR 52.40; calculated MR 52.57.

Found %: C 25.06; 25.16; H 3.20; 3.09 $C_5H_8Cl_4S$. Calculated %: C 24.80; H 3.30.

Dimethyl 2,2'-Dithiodibutyrate. A mixture of 12.5 g of 1,1-dichloro-1-butene and 30 ml of concentrated sulfuric acid was mixed vigorously at 20° while 7 g of S_2Cl_2 was added dropwise over a period of 30 minutes. During the addition hydrogen chloride was evolved, and toward the end the whole of the dichlorobutene went into solution. The reaction mixture was heated at 40-45° for five minutes, cooled, and poured into cold water. The oil that separated was extracted with chloroform, and the extract was washed with sodium hydroxide solution. The alkaline solution was acidified with hydrochloric acid and extracted with chloroform. The solution was dried, solvent was removed under vacuum, and the residue (8.5 g) was dissolved in 50 ml of methanol containing 2 ml of sulfuric acid. The methanolic solution was heated for eight hours. Vacuum distillation gave 6.5 g of dimethyl 2,2'-dithiodibutyrate; b.p. 146-148° (8 mm); $n^{20}D$ 1.4945; d^{20}_4 1.461 found MR 67.62; calculated MR 67.69.

Found %: C 45.23; 45.22; H 6.21; 6.41; S 23.85; 24.12 $C_{10}H_{18}O_4S_2$. Calculated %: C 45.11; H 6.76; S 24.05.

Reaction of 1,1,5-Trichloro-1-pentene with S_2Cl_2 in presence of Sulfuric Acid. A mixture of 35 g of 1,1,5-trichloro-1-pentene and 100 g of concentrated sulfuric acid (92%) was stirred vigorously while 14 g of S_2Cl_2 was added dropwise over a period of 40-60 minutes. Vigorous evolution of hydrogen chloride occurred at 15-18°. When the addition of S_2Cl_2 was complete, the resulting dark-brown solution was stirred for 15 minutes at 20° and for 5 minutes at 40-45°. The cooled reaction mixture was poured into water, and the thick oil was extracted with chloroform. The chloroform extract was washed with sodium hydroxide solution. The alkaline solution was acidified with hydrochloric acid, and the oil that separated was extracted with chloroform. We obtained 31 g of acidic reaction products as a thick dark-brown oil. Esterification was carried out with methanol in presence of sulfuric acid. Vacuum distillation gave a little methyl 2-chlorovalerate and 20.6 g of dimethyl 2,2'-dithiobis-5-chlorovalerate; b.p. 198-200° (1 mm); $n^{20}D$ 1.5321; d^{20}_4 1.2803; found MR 87.04; calculated MR 86.76.

Found %: C 39.88; 39.91; H 5.40; 5.38; Cl 19.68; 19.78 $C_{12}H_{20}Cl_2O_4S_2$. Calculated %: C 39.66; H 5.50; Cl 19.53.

Dimethyl 2,2'dithiobis-5-chlorovalerate (18 g) was reduced with amalgamated aluminum in moist ether. We obtained 13.2 g of methyl 5-chloro-2-mercaptovalerate; b.p. 107-108° (8 mm); $n^{20}D$ 1.4902; d^{20}_4 1.1933; found MR 44.23; calculated MR 44.23.

Found %: C 39.65; 39.68; H 5.92; 5.92 $C_6H_{11}ClO_2S$. Calculated %: C 39.44; H 6.02.

Methyl 5-chloro-2-mercaptovalerate (5 g) was dissolved in 15% sodium hydroxide solution; there was appreciable evolution of heat. After a few minutes the solution was acidified and extracted with chloroform.

We obtained 2.5 g of tetrahydro-2-thiophenecarboxylic acid, m.p. 51-52° (from petroleum ether) (the literature [7] gives m.p. 51°). The substance gave no depression of melting point in admixture with a known sample of tetrahydro-2-thiophenecarboxylic acid (see below).

The crude 2,2'-dithiobis [5-chlorovaleric acid] (20 g) was reduced as a solution in 100 ml of acetic acid at 40-50° with zinc and hydrochloric acid. The resulting 5-chloro-2-mercaptovaleric acid could not be vacuum-distilled because vigorous evolution of hydrogen chloride occurred and a mixture of the mercapto acid and tetrahydro-2-thiophenecarboxylic acid came over. The tetrahydro-2-thiophenecarboxylic acid was frozen out, and the residue was heated to 150-160° until the evolution of hydrogen chloride ceased. In all we obtained 11.5 g of tetrahydro-2-thiophenecarboxylic acid, m.p. 51-52°.

Tetrahydro-2-thiophenecarboxylic Acid. A solution of sodium 2,5-dichlorovalerate (from 8.6 g of the acid) and 6 g of $Na_2S \cdot 9H_2O$ in 30 ml of water was boiled for 30 minutes; when cool, it was acidified with hydrochloric acid and extracted with chloroform. Vacuum distillation gave 5.3 g of tetrahydro-2-thiophenecarboxylic acid, b.p. 110-111° (2 mm) and m.p. 51-52°.

Found %: C 45.28; 45.33; H 6.15; 6.12 $C_5H_8O_2S$. Calculated %: C 45.45; H 6.06.

7-Chloro-2-mercaptoheptanoic Acid. Reaction between 42 g of 1,1,7-trichloro-1-heptene, 13.5 g of S_2Cl_2, and 120 ml of concentrated sulfuric acid was carried out as in the case of 1,1,5-trichloro-1-pentene. We obtained 38.5 g of crude 2,2'-dithiobis[7-chloroheptanoic acid]. Reduction of this with zinc and hydrochloric acid in acetic acid solution gave a little 7-chloroheptanoic acid and 26.4 g of 7-chloro-2-mercaptoheptanoic acid; b.p. 144-146° (1 mm); $n^{20}D$ 1.5010; d^{20}_4 1.1941; found MR 48.48; calculated MR 48.58.

Found %: C 42.88; 42.82; H 6.55; 6.53 $C_7H_{13}ClO_2S$. Calculated %: C 42.79; H 6.61.

Methyl 7-chloro-2-mercaptoheptanoate had b.p. 107-108° (1 mm); $n^{20}D$ 1.4830; d^{20}_4 1.1309; found MR 53.16; calculated MR 53.32.

Found %: C 45.55; 45.45; H 7.07; 7.04 $C_8H_{15}ClO_2S$. Calculated %: C 45.60; H 7.12.

SUMMARY

1. In presence of anhydrous ferric chloride S_2Cl_2 adds readily to $RCH = CCl_2$ with formation of $(RC\overset{S-}{\underset{}{|}}HCCl_3)_2$. The addition of SCl_2 gives the same disulfides, and simultaneous chlorination of the $CCl_2 = CH$ group occurs.

2. Addition on S_2Cl_2 to $RHC = CCl_2$ in a medium of sulfuric acid proceeds as a "conjugated" reaction and results in the formation of α,α'-dithio dicarboxylic acids $(RCH\overset{}{\underset{S-}{|}}COOH)_2$.

3. When heated, 5-chloro-2-mercaptovaleric acid loses hydrogen chloride and is converted into tetrahydro-2-thiophenecarboxylic acid.

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ORGANOBORON COMPOUNDS

COMMUNICATION 24.* ACTION OF ACETIC ACID AND OF ACETIC ANHYDRIDE ON DICHLOROPHENYL-AND CHLORODIPHENYL-BORINES

B. M. Mikhailov and N. S. Fedotov

The chemical properties of aryldichloroborines (areneboronic dichlorides) have received very little study. Michaelis made a systematic investigation of the behavior of aryldichloroborines toward water, with which they react with formation of areneboronic acids [1], and he studied the action of alcohol [2] and chlorine [3] on dichlorophenylborine and the action of sodium methoxide and ethoxide on dichloro-2-naphthylborine [1]. There is even less information on the properties of diarylchloroborines (diarylborinic chlorides). Michaelis investigated only the action of water on chlorodiphenylborine, and he erroneously assumed that his product (m.p. 264-267°) was diphenylborinic acid [1], which actually has m.p. − 35° [4].

As we now had a simple method of preparing the previously difficultly accessible aryldichloroborines [5] and diarylchloroborines [6] at our disposal, we studied the action of acetic acid and of acetic anhydride on dichlorophenyl- and chlorodiphenyl-borines. By the action of acetic acid on dichlorophenylborine we might expect to obtain the mixed anhydride of acetic and benzeneboronic acids, diacetoxyphenylborine (I):

$$C_6H_5BCl_2 + 2CH_3COOH = C_6H_5B(OCOCH_3)_2 + 2HCl. \quad (I)$$

However, reaction between dichlorophenylborine and two molecular proportions of acetic acid gave not the anhydride (I), but a mixed anhydride on acetic and diphenylpyroboronic acids, oxybis[acetoxyphenylborine] (II). This compound could be formed by the elimination of acetic anhydride from two molecules of diacetoxyphenylborine (I):

$$C_6H_5-\underset{\underset{OCOCH_3}{|}}{B}-O-\underset{\underset{OCOCH_3}{|}}{B}-C_6H_5. \quad (II)$$

Treatment of dichlorophenylborine with acetic anhydride also gives oxybis[acetoxyphenylborine] (II):

$$C_6H_5BCl_2 + 2(CH_3CO)_2O \rightarrow C_6H_5-\underset{\underset{OCOCH_3}{|}}{B}-O-\underset{\underset{OCOCH_3}{|}}{B}-C_6H_5.$$

Chlorodiphenylborine behaved in a quite unexpected way with acetic acid. Instead of the "normal" product, acetoxydiphenylborine, oxybis[acetoxyphenylborine] (II) was obtained:

$$(C_6H_5)_2BCl \xrightarrow{CH_3COOH} \text{(II)}.$$

On the other hand, when chlorodiphenylborine was treated with acetic anhydride, the expected mixed anhydride, acetoxydiphenylborine (III), was obtained:

*Communication 23: see Bull. Acad. Sci. USSR, Div. Chem. Sci. 1958, 777.

$$(C_6H_5)_2BCl + (CH_3CO)_2O = (C_6H_5)_2BOCOCH_3 + CH_3COCl.$$
(III)

With the object of determining the mechanism of the formation of the anhydride (II) in the reaction between chlorodiphenylborine and acetic acid we studied the action of acetic acid on the anhydride (III). It was found that this anhydride is then converted into oxybis[acetoxyphenylborine] (II):

$$2(C_6H_5)_2BOCOCH_3 + 2CH_3COOH = C_6H_5-\underset{\underset{OCOCH_3}{|}}{B}-O-\underset{\underset{OCOCH_3}{|}}{B}-C_6H_5 + 2C_6H_6 + (CH_3CO)_2O.$$

When treated with acetic acid, dichloro(p-chlorophenyl)borine was converted into the mixed anhydride of acetic and bis-p-chlorophenylpyroboronic acids, oxybis[acetoxy(p-chlorophenyl)borine] (IV):

$$p\text{-}ClC_6H_4BCl_2 + 2CH_3COOH \rightarrow p\text{-}ClC_6H_4-\underset{\underset{OCOCH_3}{|}}{B}-O-\underset{\underset{OCOCH_3}{|}}{B}-p\text{-}ClC_6H_4. \quad (IV)$$

EXPERIMENTAL

All experiments were carried out in an atmosphere of nitrogen.

Action of Acetic Acid on Dichlorophenylborine. An ethereal solution of 1 g (0.02 mole) of acetic acid was added slowly to a solution of 1.7 g (0.01 mole) of dichlorophenylborine [5]. Colorless needles were precipitated and were filtered off and vacuum-dried. The product (1.08 g; 64.3%) was oxybis[acetoxyphenylborine]. In a sealed capillary the substance softened at 175° and melted at 177-178° (with decomposition).

Found %: C 62.07; H 5.24; B 7.11 $C_{16}H_{16}B_2O_5$. Calculated %: C 61.93; H 5.16; B 6.98.

Action of Acetic Anhydride on Dichlorophenylborine. A solution of 4.24 g (0.04 mole) of acetic anhydride in 10 ml of dry ether was added slowly to a solution of 3.3 g (0.02 mole) of dichlorophenylborine [5] in 20 ml of dry ether. A precipitate of colorless needles formed in 10-15 minutes; it was filtered off and vacuum-dried. The product (2.33 g; 72.4%) was oxybis[acetoxyphenylborine]. It softened at 175° and melted with decomposition at 177-178°; there was no depression of melting point in admixture with the product of the preceding experiment.

Found %: B 7.01 $C_{16}H_{16}B_2O_5$. Calculated %: B 6.93.

Action of Acetic Anhydride on Chlorodiphenylborine. A solution of 2.5 g (0.01 mole) of chlorodiphenylborine [6] in 20 ml of dry ether was introduced into a 50-ml three-necked flask fitted with reflux condenser, dropping funnel, and tube for the introduction of nitrogen. A solution of 1.3 g (0.01 mole) of acetic anhydride in 5 ml of dry ether was added slowly. After 10-15 minutes a colorless finely-crystalline precipitate formed in the ethereal solution; it was filtered off and dried. The product was 1.92 g (64%) of acetoxydiphenylborine. In a sealed capillary it softened at 107° and melted with decomposition at 113-116°.

Found %: C 75.11; H 5.99; B 4.92 $C_{14}H_{13}BO_2$. Calculated %: C 75.06; H 5.84; B 4.83.

Action of Acetic Acid on Chlorodiphenylborine. A solution of 0.75 g (0.01 mole) of acetic acid in 5 ml of dry ether was added slowly to a solution of 2.4 g (0.01 mole) of chlorodiphenylborine [6] in 15 ml of dry ether. The precipitate, which formed after 10-15 minutes as colorless needles, was filtered off and vacuum-dried. The product (1.18 g); 63.4%) was oxybis[acetoxyphenylborine]. In a sealed capillary it softened at 175° and melted with decomposition at 177-178°. There was no depression of melting point in admixture with known oxybis[acetoxyphenylborine].

Found %: B 6.86 $C_{16}H_{16}B_2O_5$. Calculated %: B 6.98.

Action of Acetic Acid on Acetoxydiphenylborine. Acetoxydiphenylborine (1 g) was dissolved by heating it with 35 ml of dry ether, and 2.5 g (an eightfold excess) of acetic acid was added. After 10-15 minutes colorless needless of oxybis[acetoxyphenylborine] (0.3 g; 40%) separated from the ethereal solution. In a sealed capillary the product melted with decomposition at 177-178°, and there was no depression of melting point in admixture with known oxybis[acetoxyphenylborine].

Found %: B 6.99 $C_{16}H_{16}B_2O_5$. Calculated %: B 6.98.

Action of Acetic Anhydride on Dichloro(p-chlorophenyl)borine. An ethereal solution of 1.2 g (0.02 mole) of acetic acid was added to a solution of 2 g (0.01 mole) of dichloro(p-chlorophenyl)borine [5] in 20 ml of dry ether. The precipitate of colorless needles was filtered off and dried under nitrogen. The product (1.33 g; 70%) was oxybis[acetoxy(p-chlorophenyl)borine]. In a sealed capillary it softened at 172° and melted with decomposition at 195-200°.

Found %: C 50.78; H 3.63; B 5.94; Cl 18.79 $C_{16}H_{14}B_2O_5Cl_2$. Calculated %: C 50.73; H 3.72; B 5.71; Cl 18.75.

SUMMARY

1. Treatment of dichlorophenylborine with acetic acid or acetic anhydride gives oxybis[acetoxyphenylborine].

2. Chlorodiphenylborine reacts with acetic anhydride with formation of acetoxydiphenylborine.

3. When chlorodiphenylborine is treated with acetic acid, at first acetoxydiphenylborine is formed and, by further reaction with acetic acid, this is then converted into oxybis[acetoxyphenylborine].

4. Dichloro(p-chlorophenyl)borine reacts with acetic acid with formation of oxybis[acetoxy(p-chlorophenyl)borine].

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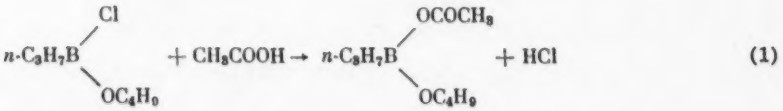
ORGANOBORON COMPOUNDS

COMMUNICATION 25. ACTION OF ORGANIC ACIDS ON BUTYL 1-PROPANECHLOROBORONATE

B. M. Mikhailov and T. A. Shchegoleva

Reaction between equimolecular amounts of organoboron esters and phosphorus pentachloride gives arenechloroboronic [1] and alkanechloroboronic [2] esters. The chemical properties of this new type of organoboron compound has as yet received little study. The reactions of arenechloroboronic esters with organomagnesium compounds [3] and amines [4] have been investigated. In the present communication we report the results of an investigation on the reactions between butyl 1-propanechloroboronate (I) and organic acids.

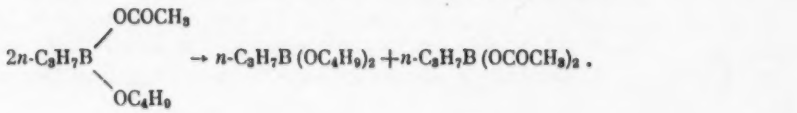
In the reaction of acetic acid with the 1-propanechloroboronic ester one might expect to obtain the mixed anhydride (II)



(1)

(I) (II)

or its symmetrization products, dibutyl 1-propaneboronate (III) and diacetoxypropylborine (IV)

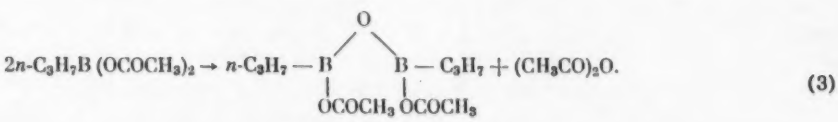


(2)

(III) (IV)

Study of the reaction showed that its course is more complex than this, the transformations represented by Equations (1) and (2) being only the first stages. Among the reaction products from butyl 1-propanechlorobonate and acetic acid (0.14 mole of each) we found only one of the expected substances, namely dibutyl 1-propaneboronate (III), and this was obtained not in the amount corresponding to Equations (1) and (2), but in a considerably smaller amount (0.036 mole). In addition we isolated 0.042 mole of oxybis[acetoxypropylborine] (V), butyl chloride (0.036 mole), butyl acetate (0.01 mole), and about one-third of the original acetic acid.

Oxybis[acetoxypropylborine] (V) was evidently formed by the elimination of acetic anhydride from diacetoxypropylborine (IV), which arose by the symmetrization of the mixed anhydride (II):



(3)

(V)

The same mechanism probably operates in the formation of oxybis[diacetoxyborine] $(CH_3COO)_2B-O-B(OCOCH_3)_2$, in the reactions between acetic anhydride and boric acid and between acetic acid and boron trichloride [5]. In this case triacetoxyborine is probably formed at first, and this then loses acetic anhydride.

Since the amount of oxybis[acetoxypropylborine] formed in the reaction is more, and that of dibutyl-1-propaneboronate is less, than that required by Equations (2) and (3), and also acetic anhydride formed by Equation (3) is absent from the reaction products, it is natural to assume that the above reactions are accompanied by further reaction between 1-propaneboronic ester (III) and acetic anhydride. Experiment showed that these substances react together only when heated, but in presence of hydrogen chloride they react at room temperature. As a result of the reaction the ester (III) is converted into oxybis[acetoxypropylborine] (V) (the yield of this was 82%), and, together with this, acetyl chloride, butyl acetate, acetic acid, and a little butyl chloride are formed.

The mechanism of this reaction, which has to explain how all these substances arise, can evidently be represented by the following successive processes. In the first stage acetic anhydride and hydrogen chloride give acetic acid and acetyl chloride [6]:

$$(CH_3CO)_2O + HCl \rightarrow CH_3COOH + CH_3COCl. \qquad (4)$$

The acetic acid formed then reacts with the ester according to the following equation:

$$2n\text{-}C_3H_7B(OC_4H_9)_2 + 4CH_3COOH \rightarrow (n\text{-}C_3H_7BOCOCH_3)_2O + 4C_4H_9OH + (CH_3CO)_2O \qquad (5)$$

With hydrogen chloride, the butyl alcohol formed in Reaction (5) gives butyl chloride, removal of water being effected by acetyl chloride formed according to Equation (4); at the same time butyl alcohol reacts with acetyl chloride with formation of butyl acetate:

$$\left.\begin{aligned} C_4H_9OH + HCl &\rightarrow C_4H_9Cl + H_2O \\ CH_3COCl + H_2O &\rightarrow CH_3COOH + HCl \end{aligned}\right\} \qquad (6)$$

$$C_4H_9OH + CH_3COCl \rightarrow CH_3COOC_4H_9 + HCl \qquad (7)$$

The whole complex of transformations occurring in the reaction of 1-propaneboronic ester with acetic anhydride in presence of hydrogen chloride evidently occurs also in the reaction between the ester and acetic acid, in the first stages of which both the acetic ester and also acetic anhydride and hydrogen chloride arise (Equations (1), (2), and (3)). As a result of Reactions (4) and (5), the amount of 1-propaneboronic ester (III) obtained by Equation (2) is reduced by 33.3%, and the amount of oxybis[acetoxypropylborine] (V) obtained by Equation (5) is raised by 16.7%. The over-all equation of the reaction is as follows:

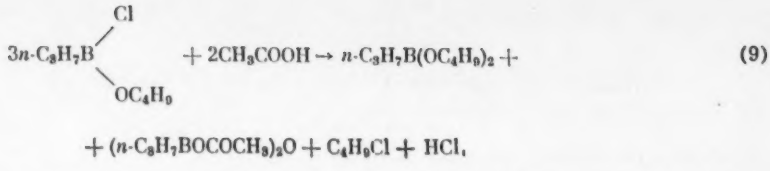
$$3n\text{-}C_3H_7B\begin{matrix}Cl\\ \diagdown\\ \diagup\\ OC_4H_9\end{matrix} + 3CH_3COOH \rightarrow n\text{-}C_3H_7B(OC_4H_9)_2 + \qquad (8)$$

$$+ (n\text{-}C_3H_7BOCOCH_3)_2O + CH_3COCl + C_4H_9OH + 2HCl,$$

which is supplemented by Equations (6) and (7).

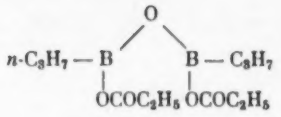
The relative amounts of butyl chloride and butyl acetate formed by Equations (6) and (7) are determined by the reaction conditions. When the reaction mixture contains a large amount of acetyl chloride and relatively little hydrogen chloride (as in the reaction between 1-propaneboronic ester and acetic anhydride, in which the hydrogen chloride introduced into the reaction mixture is used up mainly in Reaction (4)), much butyl acetate (Equation (7)) and little butyl chloride are obtained. In the reaction between 1-propaneboronic ester (I) and acetic acid the reaction mixture contains relatively more hydrogen chloride, so that more butyl chloride is formed and the acetyl chloride is therefore used up in the removal of water (Equation (6)).

If we neglect the formation of butyl acetate, of which very little is formed (about one-quarter of the amount of butyl chloride), in the reaction between 1-propaneboronic ester and acetic acid, then the reaction can be represented by the following equation:



According to this equation, three molecules of the chloroboronate requires two of acetic acid. In the experiments the ratio of the molar quantities of the chloroboronate and acetic acid that reacted was 3 : 2.3. When it is considered that in the isolation of this acid from the reaction mixture losses are unavoidable, it must be acknowledged that this ratio is in good agreement with Equation (9).

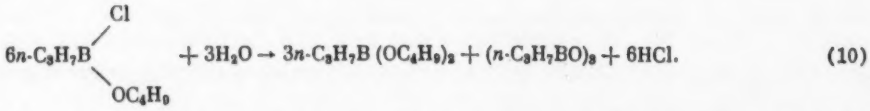
Reaction between butyl 1-propanechloroboronate and propionic acid proceeds similarly. The products are 1-propaneboronic ester, oxybis[(propionyloxy)propylborine] (VI), butyl chloride, and a little butyl propionate.



(VI)

Oxybis[acetoxypropylborine] (V) and oxybis[(propionyloxy)propylborine] (VI) are the first mixed anhydrides of alkaneboronic and aliphatic acids to be prepared.

An attempt was made to prepare dibutyl dipropylpyroboronate. For this purpose, the 1-propanechloroboronic ester was treated with water in the proportion of 1 mole per 2 moles of ester. As a result, instead of the expected dipropylpyroboronic ester, we obtained a mixture of 1-propaneboronic anhydride and dibutyl 1-propaneboronate in the molar ratio of 1 : 3. The reaction is expressed by the equation:



(10)

It should be noted that the two organoboron products have very close boiling points. 1-Propaneboronic anhydride, which we prepared by the action of thionyl chloride on 1-propaneboronic acid, has b.p. 59-61° (2 mm), whereas dibutyl 1-propaneboronate boils at 59-60° (2 mm). Hence, the narrow fraction (59-61°) (2 mm)) obtained in the reaction of water on 1-propanechloroboronic ester corresponded in analysis to the required dipropylpyroboronic ester, and only the molecular weight determination showed that it was not a pure substance, but a mixture of an ester and an anhydride.

EXPERIMENTAL

All operations with organoboron compounds were carried out in an atmosphere of nitrogen.

Action of Acetic Acid on Butyl 1-Propanechloroboronate. Butyl 1-propanechloroboronate [2] (23 g; 0.14 mole) was stirred in a four-necked flask fitted with dropping funnel, inlet tube for the passage of nitrogen, and outlet tube, and over a period of six hours 8.5 g (0.14 mole) of glacial acetic acid was added. Hydrogen chloride was evolved; the reaction mixture was not at first homogeneous, but became so after one half of the acetic acid had been added. When the whole of the acid had been added the reaction mixture was cooled. The precipitate which then formed was filtered off and washed with isopentane. The product, amounting to 10.3 g (0.042 mole), was oxybis[acetoxypropylborine], m.p. 68-74°.

Found %: C 49.58; 49.38; H 8.38; 8.41; B 9.10; 9.06. $C_{10}H_{20}B_2O_5$. Calculated %: C 49.65; H 8.33; B 8.95.

Fraction distillation of the filtrate gave the following fractions: Fraction I, b.p. 75-80°; 3.3 g; Fraction II, b.p. 113-120°; 3.2 g; Fraction III, b.p. 58-60° (2 mm); 8.5 g, Fraction IV, b.p. 105-109° (2 mm); 1 g.

Fraction I was butyl chloride (0.036 mole). After redistillation it had b.p. 77-78.5°; d^{20}_4 0.8831; $n^{20}D$ 1.4040; found MR 25.64; calculated for C_4H_9Cl MR 25.54.

Fraction II was a mixture of acetic acid and butyl acetate, which was separated by treatment with water. The mixture contained 2.1 g (0.033 mole) of acetic acid (determined by titration of the aqueous solution) and 1.0 g (0.01 mole) of butyl acetate; b.p. 122-124°; d^{20}_4 0.8822; $n^{20}D$ 1.3933; found MR 31.67; $C_6H_{12}O_2$ calculated for MR 31.56.

Fraction III was dibutyl 1-propaneboronate (0.036 mole). Thus, 26% of the original chloroboronic ester was converted into the 1-propaneboronic ester.

Found %: B 5.73; 5.79 $C_{11}H_{25}BO_2$. Calculated %: B 5.41.

Fraction IV was oxybis[acetoxypropylborine] (V), m.p. 66-71°. In all, 11.3 g of the anhydride (V) was obtained. Thus, 61% of the original chloroboronate was converted into oxybis[acetoxypropylborine].

Action of Acetic Anhydride on Dibutyl 1-Propaneboronate (in Presence of Hydrogen Chloride). Dry hydrogen chloride was passed for four hours into a mixture of 20 g (0.1 mole) of dibutyl 1-propaneboronate and 30.6 g (0.3 mole) of acetic anhydride in a two-necked flask having a gas-inlet tube and an outlet tube. After 30 minutes the reaction mixture became homogeneous; a slight rise in temperature occurred. On the next day low-boiling substances were removed from the reaction mixture; they were trapped in a receiver cooled with solid carbon dioxide. The residue was distilled. The product, amounting to 9.9 g (0.041 mole; 82%), was oxybis[acetoxypropylborine], b.p. 105-108° (2 mm) and m.p. 66-70°.

The substances that collected in the cooled receiver were fractionally distilled. We obtained 4.5 g (0.058 mole) of acetyl chloride (b.p. 49-50°), 1.2 g (0.013 mole) of butyl chloride (b.p. 77-79°; d^{20}_4 0.8866; $n^{20}D$, 0.4000; found MR 25.31; calculated for C_4H_9Cl MR 25.54), and 26.4 g of a fraction boiling in the range 116-123°, from which, by treatment with water, we separated 11.1 g (0.186 mole) of acetic acid (determined by titration) and 16.4 g (0.155 mole) of butyl acetate (b.p. 121-123°; d^{20}_4 0.8910; $n^{20}D$ 1.3957; found MR 31.30; calculated for $C_6H_{12}O_2$ MR 31.56.

Action of Propionic Acid on Butyl 1-Propanechloroboronate. Butyl 1-propanechloroboronate (31.4 g; 0.193 mole) was stirred in a four-necked flask fitted with stirrer, dropping funnel, inlet tube for nitrogen, and outlet tube while 14.3 g (0.193 mole) of propionic acid was added over a period of four hours. Hydrogen chloride was evolved. The emulsion formed at first became homogeneous after the addition of one-half of the propionic acid. When the addition was complete, the reaction mixture was fractionally distilled. The products were 5.3 g (0.058 mole) of butyl chloride, b.p. 76-77.5°, 2.4 g (0.032 mole) of propionic acid, b.p. 136-139°, 1 g (0.008 mole) of butyl propionate, b.p. 145-147°, 10.7 g (0.0505 mole) of dibutyl 1-propaneboronate, b.p. 59-61° (2 mm).

Found %: B 5.63; 5.56 $C_{11}H_{25}BO_2$. Calculated %: B 5.41.

and 13.2 g (0.0490 mole) of oxybis[(propionyloxy)propylborine], b.p. 109-112° (2 mm) and m.p. 15-25°.

Found %: C 53.66; 53.61; H 9.02; 9.02; B 7.65; 7.63. $C_{12}H_{24}B_2O_5$. Calculated %: C 53.39; H 8.96; B 8.02.

Action of Water on Butyl 1-Propanechloroboronate. Butyl 1-propanechloroboronate (11 g; 0.0675 mole) was stirred in a four-necked flask fitted with stirrer, dropping funnel, inlet tube for nitrogen, and outlet tube while 0.61 g (0.034 mole) of water dissolved in a mixture of 10 ml of dry ether and 5 ml of dry acetone was added over a period of 2.5 hours. When the addition was complete, solvent was removed and the residue was distilled. A product of b.p. 59.5-62° (2 mm) (8.5 g) was obtained; it was found to be a mixture of 1-propaneboronic anhydride and dibutyl 1-propaneboronate in the molar ratio of 1 : 3.

Found %: C 62.16; 62.32; H 11.99; 11.90; B 8.13; 8.04; found M 197.4; 196.6.

$(C_3H_7BO)_3$. Calculated %: C 51.54; H 10.09; B 15.47; calculated M 209.8.

$C_{11}H_{25}BO_2$. Calculated %: C 66.01; H 12.59; B 5.41; calculated M 200.1
$(C_3H_7BOC_4H_9)_2O$. Calculated M 270.

1-Propaneboronic Anhydride. Thionyl chloride (71 g; 0.6 mole) was added to 17.6 g (0.2 mole) of 1-propaneboronic acid in a two-necked flask fitted with inlet tube for nitrogen and reflux condenser. The mixture frothed, and there was a spontaneous drop in temperature. When the frothing stopped, the reaction mixture was heated in a water bath for two hours. When the mixture was cool, excess of thionyl chloride was removed at the water pump and the residue was distilled. We obtained 9.3 g (67%) of 1-propaneboronic anhydride; b.p. 59-61° 2 mm); d^{20}_4 0.8864; $n^{20}D$ 1.4105.

Found %: C 51.40; 51.30; H 9.99; 9.84; B 15.08; 15.25 C_3H_7BO. Calculated %: C 51.54; H 10.09; B 15.47.

SUMMARY

1. In the reaction of acetic acid with butyl 1-propanechloroboronate, dibutyl 1-propaneboronate, oxybis-[acetoxypropylborine], butyl chloride, and butyl acetate are formed.

2. In the reaction of propionic acid with butyl 1-propanechloroboronate, dibutyl 1-propaneboronate, oxybis-[(propionyloxy)propylborine], butyl chloride, and butyl propionate are formed.

3. The mechanism of the reactions between organic acids and 1-propanechloroboronic ester was elucidated.

4. Dibutyl 1-propaneboronate reacts with acetic anhydride in presence of hydrogen chloride with formation of oxybis[acetoxypropylborine], butyl acetate, butyl chloride, and acetyl chloride.

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COMPARATIVE STUDY OF THE CATALYTIC PROPERTIES OF PLATINUM UNDER THE CONDITIONS FOR THE AROMATIZATION OF GASOLINE IN PRESENCE OF HYDROGEN AT ORDINARY AND ELEVATED PRESSURES

Kh. M. Minachev, N. I. Shuikin and V. L. Vinogradov

In recent years we have devoted much attention to the catalytic properties of Pt, Pd, Rh, Ru, Ni, and Co catalysts on various carriers in the reactions of hydrocarbons of various classes [1-10]. In the course of this work we made a fairly detailed investigation of the activity and stability of catalysts of low metal content under the conditions for the aromatization of unfractionated gasolines and gasoline fractions both under laboratory conditions and under the conditions of large-scale industrial experiments. As a result of these investigations we succeeded in establishing various relationships characterizing the dependence of the activity and stability of catalysis based on Group VIII metals, on their metal contents, the methods of preparation, and the conditions of use. The use of these relationships makes it possible to make a rational choice of catalysts for the hydrogenation and dehydrogenation of hydrocarbons, and it has already considerably extended the application of expensive platinum in industrial catalysis, which has become feasible because of the great reduction in the amount of platinum contained in the catalysts. An important achievement in our investigations was the application of low-platinum catalysts in the manufacture of toluene and aviation gasolines [9,10] by the method developed by Zelinskii and Shuikin.

As a result of investigations on the transformations of individual hydrocarbons and their natural mixtures (unfractionated gasolines and various gasoline fractions) in presence of Pt, Pd, Rh, and Ru [11-15] deposited on alumina, silica, and aluminum silicate at high temperatures in presence of hydrogen at high pressures in a flow system, it was shown that under the given conditions (450-480° and 25-50 atm of hydrogen) these hydrocarbons undergo profound changes which are observed either not at all or very slightly indeed at 300° and atmospheric pressure. In these investigations new data were obtained on the direction and character of the transformations of cycloalkanes and paraffins and on the stabilities of catalysts in reaction under a pressure of hydrogen.

In the present work our task was the investigation of the activity and stability of 4% platinized charcoal under the conditions for the aromatization of a gasoline fraction at atmospheric pressure and various temperatures and also of the activity and stability of 0.8% platinized charcoal under the conditions for the aromatization of the same fraction at high temperatures in presence of hydrogen at high pressure with the object of comparing the results. The platinum content of the catalyst intended for work at atmospheric pressure was set at a higher level (4%) than that of the catalyst for aromatization at high pressure (0.8%) because of the danger of rapid deactivation of á Pt – C catalyst of very low metal content working in absence of a high pressure of hydrogen.

The results of the investigation showed that the most active and stable catalyst was 0.8% Pt – C working at 460° and 20 atm; it showed high productivity (76 liters of gasoline per g of Pt) (6.5 times as high as the productivity of the 4% Pt – C catalyst). Such a difference in the behavior of the two catalysts is probably to be explained by the fact that sulfur-containing organic compounds in the original fraction poison the catalyst working at atmospheric pressure at a much greater rate. The inactivating effect of these compounds on the catalyst working at a high pressure of hydrogen does not become apparent for a much longer time.

It is of interest also to note that neither catalyst brings about reactions of cyclohexanes other than

dehydrogenation, and no reactions of hydrocarbons of other classes proceed to an appreciable extent in presence of these catalysts. On the other hand, as we have shown previously [11-15], in presence of catalysts such as $Pt - SiO_2$, $Pt - Al_2O_3$, and $Pt - Al_2O_3 \cdot SiO_2$, supplementary formation of aromatic hydrocarbons occurs by the dehydrocyclization of n-alkanes and the dehydroisomerization of cyclopentanes. Hence, in the present case we have again confirmed the importance of the part played by carriers in the transformation of gasoline fractions in presence of oxide-metal catalysts.

EXPERIMENTAL

Both catalysts were prepared from activated charcoal washed free from OH^- ions and dried at 120-125°; this was impregnated with chloroplatinic acid solution of suitable concentration. The samples were allowed to stand for two hours and were dried at 120-125° for six hours; they were then reduced with electrolytic hydrogen with gradual raising of the temperature to 315-320° over a period of 12 hours. We checked the activities of the reduced catalysts by passage of 15 ml of cyclohexane at a space velocity of 0.32 $hour^{-1}$ at 300-305° in a feeble stream of electrolytic hydrogen. Both the 4% Pt – C and the 0.8% Pt – C catalysts showed high activity: dehydrogenation of cyclohexane proceeded to the extents of 98.5% and 96.0% respectively.

As our raw material we took the 89.5-126° fraction of straight-run gasolines of Volga-Urals petroleums; it had $n^{20}D$ 1.4040; d^{20}_4 0.7187 and its sulfur content was 0.017%. The group composition of the fraction was 52.7% alkanes, 14.6% cyclopentanes, 18.5% cyclohexanes, and 5.6% aromatics.

Experiments with the 4% platinized charcoal were carried out in the usual flow system at atmospheric pressure at a space velocity of 0.30 $hour^{-1}$ in a feeble stream of hydrogen at 300°, 325°, 350°, 375°, and 400°. Experiments at these temperatures were carried out successively with a given portion of catalyst. The temperature was raised by 25° as soon as the activity of the catalyst fell to a definite level. Experiments with the 0.8% platinized charcoal were also carried out in an apparatus of the flow type [12] at 460°, 20 atm of H_2, a space velocity of 1.1 $hour^{-1}$, and a molar ratio of hydrocarbons to hydrogen of 1:5. The contents of aromatic hydrocarbons in the catalyzates were determined by the sulfuric acid method. The gaseous catalysis products were analyzed in a VTI apparatus. In the study of the activity and stability of the 4% Pt – C catalyst, 100 ml of catalyst containing 0.98 g of the Pt was introduced into the reactor, and in the study of the properties of the 0.8% Pt – C catalyst, 50 ml (0.1 g of Pt) was taken.

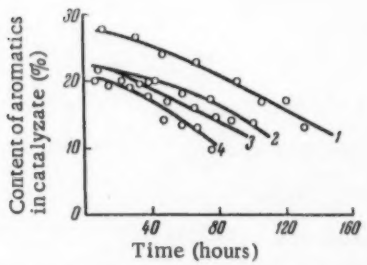

Fig. Variation of activities of catalysts with time: 1) 0.8% Pt – C, 460°, 20 atm H_2; 2) 4% Pt – C, 300°, 1 atm H_2; 3) 4% Pt – C, 350°, 1 atm H_2; 4) 4% Pt – C, 400°, 1 atm H_2.

TABLE

Results of the Investigation of Samples of Platinum Catalysts (on Charcoal Carriers) at Various Temperatures and Pressures of Hydrogen

Experiment conditions		Catalyst					
		4% Pt–C					0.8% Pt–C
Temperature of experiment (°C)		300	325	350	375	400	460
Pressure of hydrogen (atm)		Atmospheric					20
Amount of gasoline passed (ml)		3255	1170	2800	1900	2240	7600
Content of aromatic hydrocarbons in catalyzates (%)	at start of work of catalyst	22,0	18,0	22,0	20,0	20,0	27,5
	at end of work of catalyst	12,0	11,0	10,5	12,0	10,0	12,5
Duration of work of catalyst (hours)		110	39	99	64	78	152

The table summarizes the results obtained in the investigation of the two samples of platinized charcoal. The figure shows the relation of the activities of the catalysts to the length of time in operation for various temperatures.

As can be seen from the table, at all temperatures the activity of 4% Pt – C is considerably lower than that of 0.8% Pt – C, which is used in the reaction in presence of hydrogen under pressure. With successive raising of the temperature in experiments under ordinary pressure, although the activity of the 4% platinum catalyst is restored, it does not attain the level of activity of the 0.8% Pt – C catalyst. The figure shows that the activity and stability of 0.8% Pt–C in carrying out the process under 20 atm of hydrogen are considerably greater than those of 4% Pt–C working at ordinary pressure. The 4% Pt–C catalyst was in use for 390 hours, in the course of which 11.39 liters of the original fraction was passed over it, which amounts to 11.62 liters per gram of platinum. The 0.8% Pt–C catalyst carried out the aromatization of the 89.5-126° fraction of the same Volga-Urals gasoline under a pressure of 20 atm of hydrogen for a period of 152 hours, during which it aromatized 7.60 liters of the original fraction, which amounts to 76.0 liters per gram of platinum. Hence, the 0.8% Pt – C catalyst working under conditions of high pressure was more productive than the 4% Pt – C catalyst working under ordinary pressure, for in two-fifths of the time it aromatized 6.5 times as much gasoline per gram of platinum. Hence, in the aromatization of a fraction isolated from gasolines of Volga-Urals petroleum, it is more expedient to carry out the process under a pressure of hydrogen in a flow system.

SUMMARY

A comparative study was made of the catalytic properties of two platinum catalysts under the conditions for the aromatization of the 89.5-125° fraction of gasoline from Volga-Urals petroleum. It was shown that the most active and stable catalyst was one containing 0.8% of platinum on activated charcoal when used in the dehydrogenation reaction at 460° under a pressure of hydrogen of 20 atm.

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SYNTHESIS OF POLYENIC KETONES BY THE PYROLYSIS OF ACETOACETIC ESTERS

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It is known that heating of acetoacetic ester (and its homologs) with alcohols of the allyl type gives γ,δ-unsaturated ketones; the reaction is accompanied by allyl rearrangement and liberation of carbon dioxide [1]:

$$>\overset{\overset{OH}{|}}{C}-CH=CH_2 \xrightarrow[t^\circ]{CH_3COCH_2COOC_2H_5} >C=CHCH_2CH_2COCH_3 + CO_2 + C_2H_5OH.$$

In 1943 Kimel and Cope showed that acetoacetic esters of alcohols of the allyl type obtained by the action of ketene dimer on these alcohols are decarboxylated by heat with simultaneous allyl rearrangement and formation again of γ,δ-unsaturated ketones [2]:

$$>\overset{\overset{OH}{|}}{C}-CH=CH_2 \xrightarrow{(CH_2CO)_2} >\overset{\overset{OCOCH_2COCH_3}{|}}{C}-CH=CH_2 \xrightarrow[-CO_2]{t^\circ} >C=CHCH_2CH_2COCH_3$$

In 1953 Kimel [3] and in 1954 Lacey [4] found, independently, that acetoacetic esters of ethynylmethanols can also undergo pyrolysis with liberation of carbon dioxide; the products are dienones of the following structure:

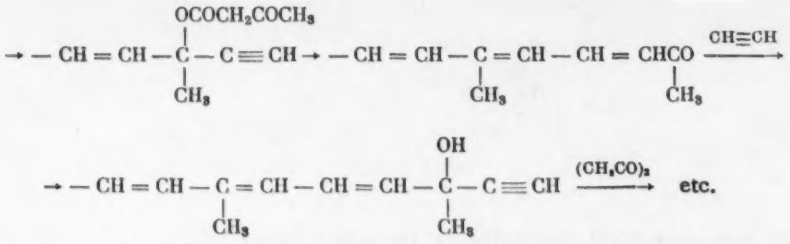
$$>\overset{\overset{OH}{|}}{C}-C\equiv CH \xrightarrow{(CH_2CO)_2} >\overset{\overset{OCOCH_2COCH_3}{|}}{C}-C\equiv CH \xrightarrow[-CO_2]{t^\circ} >C=CH-CH=CHCOCH_3$$

We became interested in the pyrolysis of acetoacetic esters of ethynylmethanols from the point of view of the application of the reaction to acetoacetic esters of enynols and polyenynols of the type

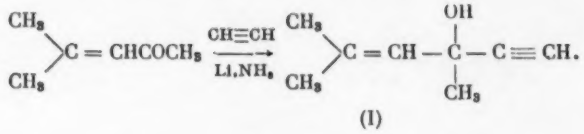
$$-CH=CH-\overset{\overset{OCOCH_2COCH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-C\equiv CH,$$

for which the reaction has not been studied at all. If it were found that pyrolysis of acetoacetic esters of this type is accompanied by intramolecular rearrangement with reaction at the acetylenic link and formation of α,β-unsaturated ketones, then it would be possible to lengthen the polyene chain with the aid of simple reactions: condensation of the α,β-unsaturated ketone with acetylene, pyrolysis of the acetoacetic ester of the resulting alcohol, condensation of the ketone formed with acetylene, and so on:

$$-CH=CH-\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{C}} \xrightarrow{CH\equiv CH} -CH=CH-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-C\equiv CH \xrightarrow{(CH_3CO)_2}$$

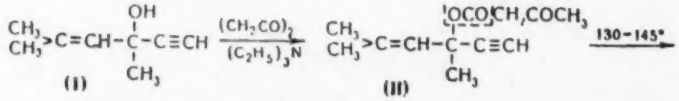


As a simple example for investigation we selected 3,5-dimethyl-4-hexen-1-yn-3-ol (I), which was prepared in 40% yield by the action of lithium acetylide on mesityl oxide in liquid ammonia solution [5]:

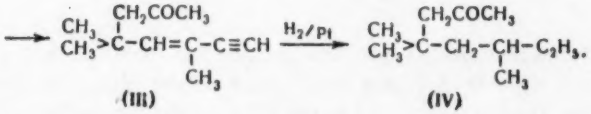


(I)

By reaction of the alcohol (I) with ketene dimer in presence of a catalytic amount of triethylamine we obtained its acetoacetic ester (II) in 68% yield:

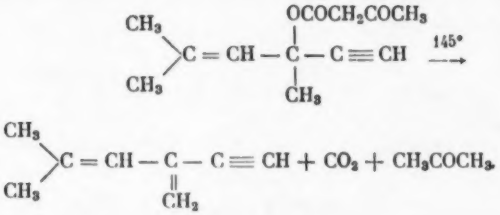


(I) (II)



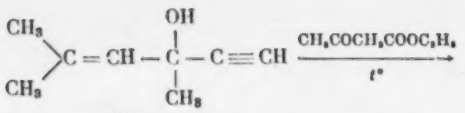
(III) (IV)

When the acetoacetic ester (II) was heated to 130-145°, it underwent pyrolysis with vigorous evolution of carbon dioxide (95% yield). The pyrolysis product contained a considerable amount of acetone, which was probably formed in a side reaction:

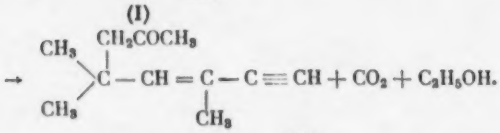


From the pyrolysis products we isolated a pure substance (b.p. 73-75° (7 mm) and $n^{20}D$ 1.4690) in 22% yield; it gave a semicarbazone of m.p. 116-117° and a positive reaction for the presence of acetylenic hydrogen with ammoniacal silver nitrate solution.

The general physical and chemical properties of this product (low boiling point, low refractive index, presence of an acetylenic bond) indicated that the pyrolysis of the acetoacetic ester (II) is accompanied by intramolecular rearrangement with participation not of the triple bond, but of the double bond, with formation of the branched acetylenic ketone (III). A similar result was obtained when the alcohol (I) was heated with ethyl acetoacetate:



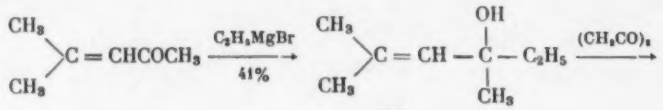
(I)



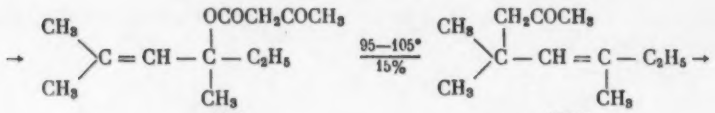
(III)

In this reaction the same unsaturated ketone (III) was obtained in 20% yield.

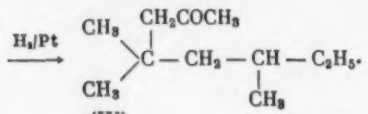
To confirm that the reaction took this course, the unsaturated ketone (III) was fully hydrogenated to the saturated ketone (IV), and a confirmatory synthesis of the ketone (IV) was carried out as follows:



(V)



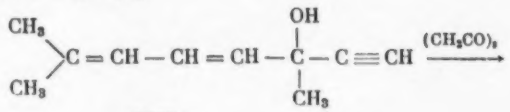
(VI) (VII)



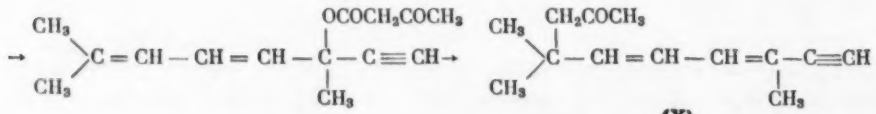
(IV)

By treatment with ethylmagnesium bromide mesityl oxide was converted in 41% yield into the alcohol (V), which by reaction with ketene dimer readily gave its acetoacetic ester (VI). This was not distilled because it decomposes at a low temperature; it was subjected to pyrolysis, and the unsaturated ketone (VII) was isolated from the products in 15% yield. Hydrogenation of the ketone (VII) gave the above-described saturated ketone (IV) prepared in the two different ways; both melted at 134-135°, and a mixture of them showed no depression.

It was of interest also to investigate the pyrolysis reaction for the case of the acetoacetic ester of 3,7-dimethyl-4,6-octadien-1-yn-3-ol (VIII), which was prepared earlier in our laboratory by the condensation of acetylene with 6-methyl-3,5-heptadien-2-one [6]:

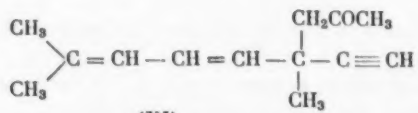


(VIII)



(X)

or



(XI)

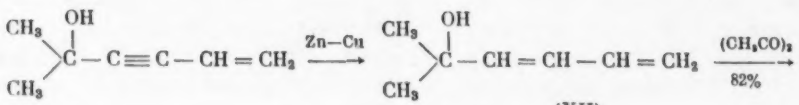
By the action of ketene dimer on the alcohol (VIII) in presence of trimethylamine we obtained the acetoacetic ester (IX), which, without being isolated, was subjected to pyrolysis at 110-140°.

Reaction was accompanied by much resinification, but we isolated a pure substance of b.p. 74-76° (0.2 mm) in 19.4% yield, and this gave a positive reaction for the presence of acetylenic hydrogen with ammoniacal silver nitrate. From the physical and chemical properties of the substance (low boiling point, low refractive index, presence of acetylenic bond) it may be concluded that it was a branched dienynone (X) or (XI).

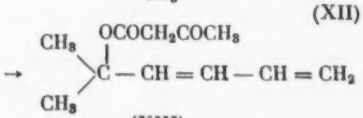
When the alcohol (VIII) was heated with ethyl acetoacetate to 135-155°, carbon dioxide was liberated (100% yield) and ethanol distilled off. Distillation gave a 23% yield of a substance having the same properties and constants of the above-described ketone (X) or (XI).

As stated above, in the pyrolysis acetoacetic esters of tertiary allyl alcohols rearrangement occurs very readily with liberation of carbon dioxide and formation of the corresponding unsaturated ketones. The pyrolysis of the acetoacetic esters of tertiary dienic alcohols has remained entirely without study until now. It was of interest to determine whether in this case pyrolysis would result in rearrangement with simultaneous shift of two double bonds and formation of the corresponding dienic ketone.

In order to resolve this question we synthesized 2-methyl-3,5-hexadien-2-ol (XII) by hydrogenation over coppered zinc [7] of 2-methyl-5-hexen-3-yn-2-ol, which is readily prepared from acetone and 1-buten-3-yne [8]:



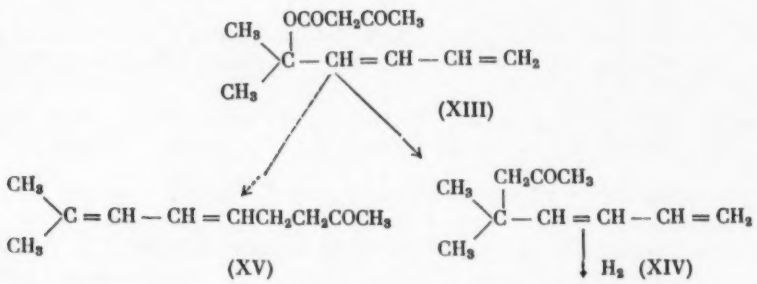
(XII)



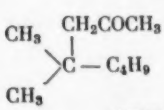
(XIII)

Treatment of the alcohol (XII) with ketene dimer in presence of a catalytic amount of triethylamine gave the acetoacetic ester (XIII) in 82% yield, and when this was heated to 145° there was a vigorous evolution of carbon dioxide. Distillation of the pyrolysis products gave a 33% yield of the dienic ketone (XIV), a colorless liquid of b.p. 68-72° (8 mm); semicarbazone, m.p. 113-114°. When hydrogenated, this ketone absorbed two molecular proportions of hydrogen and was converted into the saturated ketone (XVI), m.p. 62-64° (7 mm); semicarbazone, m.p. 106-107°.

We expected that the structure of the dienic ketone obtained in the pyrolysis of the acetoacetic ester (XIII) would be either (XV) in the case of rearrangement with shift of the two double bonds or (XIV) if such rearrangement did not occur.



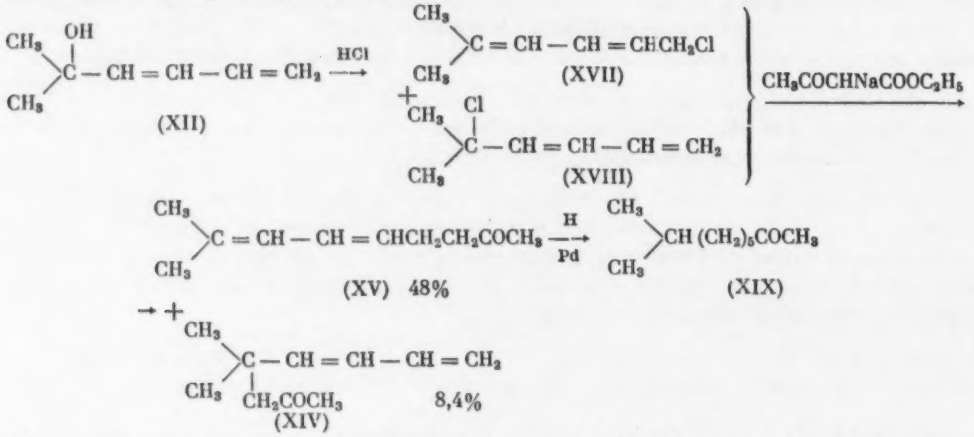
(XV) (XIV)



(XVI)

To determine the structure of the dienic ketone, the ketones (XIV) and (XV) were synthesized independently. It was shown by Nazarov and Fisher [9] that in the treatment of 2-methyl-3,5-hexadien-2-ol (XII) with hydrogen

chloride rearrangement occurs with replacement of hydroxyl by chlorine: the chlorine moves to 6-position and the main product is the dienic primary chloro compound (XVII). This rearrangement proceeds to an extent of not less than 80%, and the dienic tertiary chloro compound (XVIII) is present to an extent of not more than 20%, though we did not succeed in isolating it in the pure state.



By the action of sodioacetoacetic ester on the resulting mixture of primary and tertiary chloro compounds (XVII) and (XVIII) we obtained a mixture of the ketones (XV) and (XIV). The ketone (XV), formed as the main product (48%) yield from the dienic primary chlorocompound (XVII), had b.p. 63-65° (2.5 mm); its semicarbazone melted at 130-131°. When hydrogenated, this ketone (XV) absorbed two molecular proportions of hydrogen and was converted into 8-methyl-2-nonanone (XIX), b.p. 78-79° (7 mm); semicarbazone, m.p. 128-129°.

The ketone (XIV), obtained in small amount (8.4%) from the dienic tertiary chloro compound (XVIII), had b.p. 71-75° (10 mm); its semicarbazone had m.p. 113-114°, undepressed by admixture of the semicarbazone of the above-described ketone (XIV) obtained by the pyrolysis of the acetoacetic ester of 2-methyl-3,5-hexadien--2-ol (XIII). Hence, as a result of the pyrolysis of the acetoacetic ester (XIII) we obtained only 4,4-dimethyl-5, 7-octadien-2-one (XIV), and the dienic ketone (XV) was not formed at all.

EXPERIMENTAL

3,5-Dimethyl-4-hexen-1-yn-3-ol (I). A solution of 69 g of mesityl oxide in 400 ml of dry ether was added over a period of three hours at − 55° to lithium acetylide prepared from 9 g of lithium in 1500 ml of liquid ammonia. The mixture was stirred for three hours at about − 50° and left overnight. Ammonia was removed, and 400 ml of ether, 550 ml of water, and 90 g of ammonium chloride were added. The product was extracted with ether, washed with water, dried with magnesium sulfate, and vacuum-distilled. The following fractions were obtained:

Fraction I, boiling point 42-55° (23 mm); $n^{22}D$ 1.4480; 23.6 g
Fraction II, boiling point 67-73° (23 mm); $n^{22}D$ 1.4612; 35 g

Two fractionations of Fraction II gave 30 g of 3,5-dimethyl-4-hexen-1-yn-3-ol (I), b.p. 71-73° (21 mm) and $n^{20}D$ 1.4635. The literature [5] gives b.p. 73-74° (26 mm) and $n^{20}D$ 1.4620.

3-5-Dimethyl-4-hexen-1-yn-3-ol Acetoacetate (II). Over a period of 15 minutes 7.5 g (0.089 mole) of ketone dimer was added at room temperature to a stirred mixture of 10 g (0.081 mole) of 3,5-dimethyl-4-hexen--1-yn-3-ol (I) and five drops of triethylamine. The mixture was heated at 55-65° for 75 minutes and was then dissolved in 60 ml of ether. The solution was washed with 5% sodium carbonate solution and with water, and it was then dried with calcined magnesium sulfate. Vacuum distillation gave 11.4 g (68%) of 3,5-dimethyl-4-hexen--1-yn-3-ol acetoacetate (II); b.p. 78-80° (0.06 mm); $n^{20}D$ 1.4760; d^{20}_4 0.9968; found MR 58.82; calculated MR for the enol form 57.86, and for the keto form 56.81.

Found %: C 69.15; 69.09; H 7.90; 7.96 $C_{12}H_{16}O_3$. Calculated %: C 69.2; H 7.7.

Pyrolysis of 3,5-Dimethyl-4-hexen-1-yn-3-ol Acetoacetate (II). A flask fitted with thermometer and reflux condenser and connected to a graduated gas holder for the measurement of the gas evolved was charged with 10 g

of the acetoacetic ester (II). The flask was heated in Wood's metal, and at 135-145° vigorous evolution of gas began. In the course of 45 minutes 840 ml of carbon dioxide was evolved. The temperature in the flask then fell to 130° as a result of the formation of acetone, and the evolution of gas ceased. The reflux condenser was therefore replaced by one set for distillation, and the acetone formed (0.8 g) was distilled off (b.p. 58-60°; m.p. of the 2,4-dinitrophenylhydrazone 123-125°). The product was again heated for 20 minutes at 160-180°, and a further 310 ml of carbon dioxide was evolved. In all, 1150 ml of carbon dioxide was liberated (95% yield).

The residue in the flask (6.6 g) was dissolved in 50 ml of ether, and the solution was washed with 5% sodium carbonate solution and with water, dried, and vacuum-distilled. We obtained 1.7 g of a colorless liquid (b.p. 72-77° (7 mm) and $n^{21}D$ 1.4700)and 3.8 g of a resinous residue.

Redistillation gave 4,4,6-trimethyl-5-octen-7-yn-2-one (III) in 22% yield; b.p. 73-75° (7 mm); $n^{20}D$ 1.4690; d^{20}_4 0.8966; found MR 50.99; calculated MR 50.45.

Found %: C 80.67; 80.79; H 10.00; 9.71 $C_{11}H_{16}O$. Calculated %: C 80.41; H 9.73.

The ketone (III) gave a positive reaction for acetylenic hydrogen with ammoniacal silver nitrate. After being recrystallized from 50% ethanol, the semicarbazone of the ketone (III) melted at 116-117°.

Found %: N 19.12; 19.33 $C_{12}H_{19}ON_3$. Calculated %: N 19.00.

The ketone (III) (1.4 g)was exhaustively hydrogenated in 8 ml of absolute ethanol in presence of a platinum catalyst. The volume of hydrogen absorbed was 680 ml (20°, 735 mm), which corresponds to 3 moles of hydrogen per mole of ketone. Distillation gave the sturated ketone (IV); b.p. 69-70° (12 mm); $n^{20}D$ 1.4443; d^{20}_4 0.8539; found MR 53.01; calculated MR 53.01.

Found %: C 77.93; 77.92; H 12.49; 12.45 $C_{11}H_{22}O$. Calculated %: C 77.65; H 12.9.

The semicarbazone of the ketone (IV) had m.p. 134-135° (from 70% ethanol).

Found %: N 18.30; 18.19 $C_{12}H_{25}ON_3$. Calculated %: N 18.50.

Reaction of 3,5-Dimethyl-4-hexen-1-yn-3-ol (I) with Ethyl Acetoacetate. A mixture of 8.2 g (0.066 mole) of 3,5-dimethyl-4-hexen-1-yn-3-ol (I) and 9 g (0.103 mole) of ethyl acetoacetate was heated in a bath of Wood's metal at 140-170°. In the course of 90 minutes 4.6 ml of a liquid of b.p. 62-72° distilled off, and 1310 ml of carbon dioxide was evolved. The usual treatment and vacuum distillation gave 2.2 g (20%) of the above-described unsaturated ketone (III) (b.p. 72-75° (7 mm); $n^{20}D$ 1.4685), the semicarbazone of which melted at 116-117°.

Preparation and Pyrolysis of 3,5-Dimethyl-4-hexen-3-ol Acetoacetate (VI). Ketene dimer (8.0 g; 0.094 mole) was added dropwise at 60° to a mixture of 10.5 g (0.082 mole) of 3,5-dimethyl-4-hexen-3-ol(V)[10](b.p. 47-48° (10 mm);$n^{22}D$ 1.4462)and 4 drops of triethylamine. The mixture was stirred at this temperature for 30 minutes and was then subjected to pyrolysis. Evolution of carbon dioxide started at 80°, and the bulk of the gas was liberated at 95-105°. When 1040 ml of carbon dioxide had been liberated, the reflux condenser was replaced by one set for distillation and the acetone formed was distilled off (4.2 g of acetone, b.p. 58-60°). In all, 1850 ml (100%) of carbon dioxide was liberated in 90 minutes, and at the end of the reaction the temperature in the flask was 125-130°. After treatment as described for the previous experiment we obtained the following fractions:

Fraction I, b. p. 58-61° (95 mm); $n^{21}D$ 1.4453; 3.7 g
Fraction II, b. p. 68-70° (8 mm); $n^{21}D$ 1.4474; 2 g

Resinous residue 2 g

Fraction I., a volatile liquid, contained the dienic hydrocarbon 2,4-dimethyl-2,4-hexadiene. Fraction II was 4,4,6-trimethyl-5-octen-2-one (VII); $n^{20}D$ 1.4478; d^{20}_4 0.8598; found MR 52.34; calculated MR 52.54. The semicarbazone of the ketone (VII) melted at 128-129° (from alcohol).

Found %: N 18.53; 18.70 $C_{12}H_{23}ON_3$. Calculated %: N 18.63.

The ketone (VII) (1.65 g) was dissolved in 10 ml of absolute ethanol and hydrogenated in presence of a platinum catalyst. The volume of hydrogen absorbed was 255 ml (22°, 745 mm), which corresponds to 1.02 moles of hydrogen per mole of the substance. Distillation gave 4,4,6-trimethyl-2-octanone (IV) (b.p. 69-70° (12 mm); $n^{21}D$ 1.4440), the semicarbazone of which melted at 134-135° and showed no depression of melting

point in admixture with the sample obtained previously.

Reaction of 3,7-Dimethyl-4,6-octadien-1-yn-3-ol (VIII) with Ethyl Acetoacetate. A mixture of 5.2 g (0.034 mole) of 3,7-dimethyl-4,6-octadien-1-yn-3-ol (VIII) and 9 g (0.069 mole) of ethyl acetoacetate was heated in an atmosphere of nitrogen for one hour at 135-155°. In the course of this time 860 ml of carbon dioxide was evolved and 1.5 ml of liquid (b.p. 70-77°) distilled off. After the usual treatment the product was vacuum-distilled. We obtained 1.5 g of the ketone (X) or (XI) as a yellow liquid; b.p. 75-78° (0.25 mm); $n^{20}D$ 1.4970; d^{20}_4 0.9126; found MR 61.02; calculated MR 59.25.

Found %: C 82.20; 82.36; H 9.90; 9.77 $C_{13}H_{18}O$. Calculated %: C 82.02; H 9.54.

Resinous residue (3.8 g).

The product gave a positive reaction for acetylenic hydrogen with ammoniacal silver nitrate. The 2,4-dinitrophenylhydrazone, semicarbazone, and thiosemicarbazone of the ketone were precipitated as oils which we did not succeed in crystallizing.

Preparation and Pyrolysis of 3,7-Dimethyl-4,6-octadien-1-yn-3-ol Acetoacetate (IX). Ketene dimer (3.2 g; 0.038 mole) was added in a stream of nitrogen to a stirred mixture of 5 g (0.033 mole) of 3,7-dimethyl--4,6-octadien-1-yn-3-ol (VIII) (b.p. 87-88° (6 mm); $n^{21}D$ 1.5120) and three drops of triethylamine. The mixture was heated for 30 minutes at 60-70° and for 30 minutes at 70-85°, and it was then subjected to pyrolysis. Evolution of carbon dioxide began at 110°, and most of it was liberated in the range 110-140°. In all, 480 ml (60% yield) of carbon dioxide was liberated. At the end of the reaction the reaction the temperature was 170-180°.

After the usual treatment we obtained 1 g of a substance of b.p. 74-76° (0.2 mm) and $n^{20}D$ 1.4978. In its constants and properties the substance was identical with the ketone (X) or (XI) described in the preceding experiment. When the pyrolysis was carried out in dry petrolatum the yield of ketone was not increased.

2-Methyl-3,5-hexadien-2-ol Acetoacetate (XIII). Ketene dimer (17.6 g; 0.21 mole) was added dropwise to a stirred mixture of 20 g (0.178 mole) of 2-methyl-3,5-hexadien-2-ol (XII) (b.p. 42-43° (8 mm); $n^{22}D$ 1.4680) and five drops of triethylamine at 65°. The mixture was heated for two hours at 75-85° and then given the usual treatment. The product, amounting to 28.7 g (82%), was 2-methyl-3,5-hexadiene-2-ol acetoacetate (XIII); b.p. 77-79° (0.25 mm); $n^{20}D$ 1.4714; d^{20}_4 0.9851; found MR 54.06; calculated MR for keto for 53.73, and for enol form 54.78.

Found %: C 67.38; 67.34; H 8.43; 8.43 $C_{11}H_{16}O_3$. Calculated %: C 67.33; H 8.22.

Pyrolysis of 2-Methyl-3,5-hexadien-2-ol Acetoacetate (XIII). 4,4-Dimethyl-5,7-octadien-2-one (XIV). 2-Methyl-3,5-hexadien-2-ol acetoacetate (XIII) (12 g) was heated in a flask under reflux. At 145° vigorous evolution of gas began. In the course of 30 minutes 765 ml of carbon dioxide was evolved, and the temperature then began to fall as a result of the formation of a volatile liquid and the evolution of carbon dioxide ceased. The reflux condenser was replaced by one set for distillation, and 1.2 g of acetone (b.p. 58-60°; 2,4-dinitrophenylhydrazone, m.p. 123-124°) and 1.6 g of a liquid (b.p. 105-110° and $n^{20}D$ 1.4664) came over. In all, 1405 ml of carbon dioxide was evolved. At the end of the reaction the temperature was 180-190°. The usual treatment gave 3.1 g (33%) of 4,4-dimethyl-5,7-octadien-2-one (XIV) as a colorless liquid; b.p. 69-72° (8 mm); $n^{20}D$ 1.4610; d^{20}_4 0.9634; found MR 48.26; calculated MR 47.46.

Found %: C 78.83; 79.02; H 10.68; 10.53 $C_{10}H_{16}O$. Calculated %: C 78.91; H 10.59.

The semicarbazone of the ketone (XIV) had m.p. 113.5-114.5° (from 70% ethanol).

Found %: N 20.13; 19.74 $C_{11}H_{19}ON_3$. Calculated %: N 20.1.

The dienic ketone (XIV) (1.8 g) was hydrogenated in 10 ml of absolute ethanol in presence of a platinum catalyst. The volume of hydrogen absorbed was 575 ml (19°, 746 mm), which corresponds to 1.95 moles of hydrogen per mole of substance. Distillation gave 4,4-dimethyl-2-octanone (XVI); b.p. 62-64° (7 mm); $n^{20}D$ 1.4250; d^{20}_4 0.8256; found MR 48.41; calculated MR 48.39. The semicarbazone of the ketone (XVI) had m.p. 106-107° (from 70% methanol).

Found %: N 19.91; 19.86 $C_{11}H_{23}ON_3$. Calculated %: N 19.72.

4,4-Dimethyl-5,7-octadien-2-one (XIV) and 8-Methyl-5,7-nonadien-2-one (XV). Sodioacetoacetic ester was prepared from 2.4 g of sodium, 34 ml of ethanol, and 16.8 g (0.128 mole) of acetoacetic ester, and with stirring

at − 10°, 11.2 g (0.086 mole) of the mixture of dienic chloro compounds (XVII) and (XVIII) (b.p. 55-57° (8 mm); $n^{22}D$ 1.5075) in 15 ml of ether was added. The mixture was stirred for four hours at room temperature and for 90 minutes at 60°. Ethanol was distilled off under reduced pressure, 60 ml of 36% sodium hydroxide solution was added to the residue, and the mixture was heated for five hours at 65-70°. Under cooling with ice water the product was acidified with concentrated hydrochloric acid (28 ml); the substance was extracted with ether, washed with 5% sodium bicarbonate solution and with water, and dried with magnesium sulfate. Fractionation gave the following fractions:

Fraction I, boiling point 71-75° (10 mm); $n^{18}D$ 1.4640; 1.1 g
Fraction II, boiling point 63-65° (2.5 mm); $n^{20}D$ 1.4850; 6.3 g.

Resinous residue 3 g

Fraction I was 4,4-dimethyl-5,7-octadien-2-one (XIV), the semicarbazone of which melted at 113-114° and showed no depression in admixture with the above-described semicarbazone of the dienone (XIV) obtained by the pyrolysis of 2-methyl-3,5-hexadien-2-ol acetoacetate (XIII).

Fraction II was 8-methyl-5,7-nonadien-2-one (XV); b.p. 64-65° (2 mm); $n^{20}D$ 1.4840; d^{20}_4 0.8766; found MR 49.67; calculated MR 47.46.

Found %: C 79.13; 78.79; H 10.54; 10.54 $C_{10}H_{16}O$. Calculated %: C 78.91; H 10.59.

The semicarbazone of the ketone (XV) had m.p. 130-131° (from 80% ethanol).

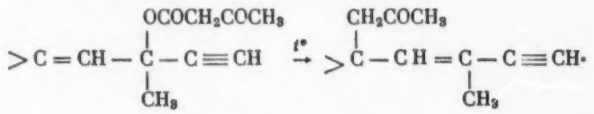
Found %: N 20.39; 20.38 $C_{11}H_{19}ON_3$. Calculated %: N 20.1.

8-Methyl-5,7-nonadien-2-one (XV) (1.2 g) was hydrogenated in 8 ml of absolute ethanol in presence of a platinum catalyst. The volume of hydrogen absorbed was 375 ml (19°, 747 mm), which corresponds to 1.95 moles of hydrogen per mole of substance. Distillation gave 8-methyl-2-nonanone (XIX); b.p. 78-79° (7 mm); $n^{20}D$ 1.4235; d^{20}_4 0.8204; found MR 48.57; calculated MR 48.39. The semicarbazone of the ketone (XIX) had m.p. 128-129° (from ethanol).

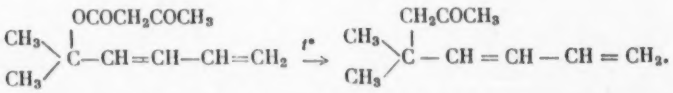
Found %: N 19.97; 19.97 $C_{11}H_{23}ON_3$. Calculated %: N 19.72.

SUMMARY

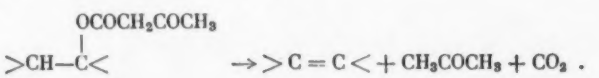
1. It was shown that the pyrolysis of acetoacetic esters of enynols is accompanied by an intramolecular rearrangement occurring in the direction of the double bond, and not the triple bond; only enynic ketones are formed; no formation of polyenic ketones occurs:



2. It was shown that the pyrolysis of 2-methyl-3,5-hexadien-2-ol acetoacetate proceeds without rearrangement of the double bonds with formation of the corresponding tertiary dienic ketone:



3. In the cases described, the pyrolysis of acetoacetic esters is accompanied by cleavage processes with formation of acetone and the corresponding hydrocarbons:



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ORGANOPHOSPHORUS POLYMERS

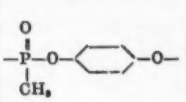
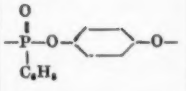
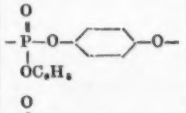
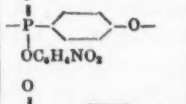
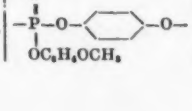
COMMUNICATION 4. HYDROQUINONE POLYESTERS OF SOME PHOSPHONIC ACIDS AND ARYL DIHYDROGEN PHOSPHATES

V. V. Korshak, I. A. Gribova, and M. A. Andreeva

We showed previously [1] that reaction between alkyl- and aryl-phosphonic dichlorides and glycols in presence of substances for binding hydrogen chloride results in the formation of polyesters. When these products are heated, thermal degradation occurs with formation of monomeric cyclic esters. The monomeric cyclic esters were found to be capable of polymerization in presence of various catalysts. With increase in the number of methylene groups in the polymer chain, the tendency for the formation of cyclic esters in the course of thermal degradation diminishes. Thus, in the case of the polyester obtained by reaction between 1,6-hexanediol and methylphosphonic dichloride, the isolation of a cyclic ester presents great difficulties.

The polymers which we prepared previously, in which, apart from oxygen and phosphorus, the chain consisted of methylene groups, were viscous liquids. The introduction of different substituents in the side chain attached to phosphorus did not affect the properties of the polymers substantially. It appeared to be of interest, therefore, to prepare phosphorus-containing polymers containing aromatic residues in the main chain. Kabachnik, Rossiiskaia, and Novikova investigated the reaction of chloromethylphosphonic dichloride with pyrocatechol [2]. They isolated and characterized products of the reaction of chloromethylphosphonic dichloride with one and with two molecules of pyrocatechol. Zentfman and Wright [3] obtained some transparent solid polymers by reaction of some phosphonic dichlorides with dihydroxy compounds.

TABLE 1

Acid	Repeating unit	Temperature (°C)		Intrinsic viscosity	Appearance of polymer
		soft-tening	thread formation		
Methylphosphonic		63—65	73—74	0,1	Brittle, clear
Phenylphosphonic		83—85	94—95	0,16	Ditto
Phenyl dihydrogen phosphate		50	Insoluble in cresol	—	Rubberlike
p-Nitrophenyl dihydrogen phosphate		36—38	41—42	0,05	Brittle, light-brown
p-Methoxyphenyl dihydrogen		35—38	—	Insoluble in cresol	Brittle, clear

We have prepared the hydroquinone polyesters of methyl- and phenyl-phosphonic acids and of phenyl, p-nitrophenyl, and p-methoxyphenyl dihydrogen phosphates. The polycondensation was carried out by heating an equimolecular mixture of the acid chloride and hydroquinone in an atmosphere of nitrogen. The nitrogen facilitated the rapid removal of the hydrogen chloride liberated in the process. The condensation conditions were as follows: 4 hours at 140°, 7 hours at 170°. 1 hour at 180°, 1 hour at 190°, and 3 hours at 200°. The catalyst (1% of tin on the weight of reactants) was added to the reaction mixture at 170°. The viscosities of the polyesters were determined on 0.5% solutions in cresol (mixture of isomers); the softening points and temperatures for thread formation were determined. The results are given in Table 1.

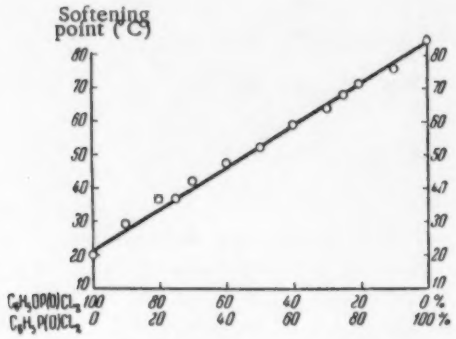


Fig. 1. Dependence on composition of the softening point of mixed polyesters obtained by reaction of HOC_6H_4OH with $C_6H_5P(O)Cl_2$ and $C_6H_5OP(O)Cl_2$.

The properties of polyesters of aryl dihydrogen phosphates are also greatly dependent on the structure of the original acid. Thus, the polyester of phenyl dihydrogen phosphate is a rubberlike substance, which does not melt, but softens at 50°. The polyesters of p-nitrophenyl and p-methoxyphenyl dihydrogen phosphates soften at lower temperatures (36-38° and 35-38°, respectively) than the polyesters of methyl- and phenyl-phosphonic acids. Hence, the replacement of the C – P bond by the C – O – P linkage in the side group results in the formation of polymers of lower softening point. Polyesters of p-nitrophenyl and and p--methoxyphenyl dihydrogen phosphates are clear solids which show good adhesion to glass; they dissolve in chloroform. The hydroquinone polyester of p-methoxyphenyl dihydrogen phosphate is insoluble in cresol. The formation of an infusible and insoluble polymer from phenyl phosphorodichloridate and hydroquinone is probably to be explained by the occurrence of exchange reactions between the phenoxy group of the acid chloride and hydroquinone. In the case of p-nitrophenyl and p-methoxyphenyl dihydrogen phosphates the rate of this reaction is lower and such products are not obtained. Hence, as we expected, the introduction of aromatic residues in the polymer chain results in a great difference in the properties of the polymer, as compared with a chain made up of methylene groups. The same is observed in the case of polyesters which do not contain phosphorus.

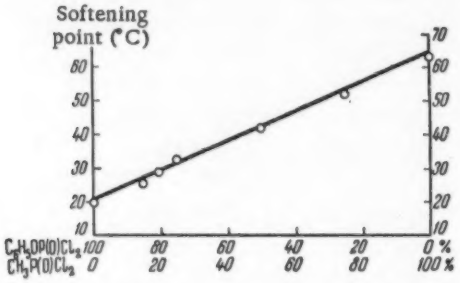


Fig. 2. Dependence on composition of the softening point of mixed polyesters obtained by reaction of HOC_6H_4OH with $CH_3P(O)Cl_2$ and $C_6H_5OP(O)Cl_2$.

We considered it to be of interest to prepare mixed polyesters containing residues of different phosphonic acids and acid phosphoric esters. The properties of mixed polyesters must be determined by the relative amounts of the reactants taken. We synthesized mixed polyesters having varying contents of the phosphonic and phosphoric residues, but with a total content of 1 mole per mole of hydroquinone. Investigation of these binary systems showed that there is a linear relationship between composition and softening point. This relationship is shown diagrammatically in Figures 1 and 2. In Table 2 and Fig. 1 we show the variation in the properties of mixed polyesters obtained from hydroquinone, phenylphosphonic dichloride, and phenyl phosphorodichloridate. As will be seen from Table 1, the polyesters from phenyl dihydrogen phosphate is a rubberlike polymer, whereas the polyester of phenylphosphonic acid is a brittle solid, softening point 83-85°. With increase in the content of residues of phenyl dihydrogen phosphate (Table 2 and Fig. 1), the softening point of the mixed polyesters falls and their properties approach those of the polyester of phenyl dihydrogen phosphate: good adhesion to glass and rubberlike properties. In the system of polyesters prepared from hydroquinone, methylphosphonic dichloride, and phenylphosphorodichloridate, the variation in the properties of the mixed polyester is analogous, but the temperatures of softening and thread formation are lower for these polyesters (Table 3 and Fig. 2).

TABLE 2

Molar proportions of reactants			Temperature (°C) of		Molar proportions of reactants			Temperature (°C) of	
	$C_6H_5P(O)Cl_2$	$C_6H_5OP(O)Cl_2$	softening	thread formation		$C_6H_5P(O)Cl_2$	$C_6H_5OP(O)Cl_2$	softening	thread formation
1	0	1	50	—	1	0,6	0,4	58—60	75—76
1	0,1	0,9	28—30	51—53	1	0,7	0,3	63—65	80—81
1	0,2	0,8	36—39	54—56	1	0,75	0,25	65—70	83—85
1	0,25	0,75	36—38	48—50	1	0,8	0,2	69—72	85—86
1	0,3	0,7	40—43	57—58	1	0,9	0,1	76—77	86—88
1	0,4	0,6	46—49	60—62	1	1	0	83—85	94—95
1	0,5	0,5	50—55	68—70					

TABLE 3

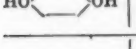
Molar proportions of reactants			Temperature (°C) of	
	$CH_3P(O)Cl_2$	$C_6H_5OP(O)Cl_2$	softening	thread formation
1	1	0	63—65	73—74
1	0,75	0,25	62—55	62—63
1	0,5	0,5	41—43	54—55
1	0,25	0,75	32—34	46—47
1	0,20	0,80	29—30	42—43
1	0,15	0,85	26—27	46—48
1	0	1	~20	—

TABLE 4

Molar proportions of reactants			Temperature (°C) of	
			softening	thread formation
HOC_6H_4OH	$C_6H_5P(O)Cl_2$	$C_6H_5OP(O)Cl_2$		
1	0	1	50	—
1	0,5	0,5	50—55	68—70
1	1	0	83—85	94—95
HOC_6H_4OH	$C_6H_5P(O)Cl_2$	$NO_2C_6H_4OP(O)Cl_2$		
1	0	1	36—38	41—42
1	0,5	0,5	67—69	—
1	1	0	83—85	94—95
HOC_6H_4OH	$C_6H_5P(O)Cl_2$	$CH_3OC_6H_4OP(O)Cl_2$		
1	0	1	35—38	—
1	0,5	0,5	63—65	81—83
1	1	0	83—85	94—95
HOC_6H_4OH	$CH_3P(O)Cl_2$	$C_6H_5OP(O)Cl_2$		
1	0	1	50	—
1	0,5	0,5	41—43	54—55
1	1	0	63—65	73—74

It was of interest to determine the effect of the nature of the group attached to phosphorus on the properties of mixed polyesters. With this object we prepared mixed polyesters in which the molar ratio of the acid chlorides was 1:1. The results of the investigation are given in Table 4, from which it can be seen that the nature of the group attached to phosphorus has an appreciable effect on the properties of the mixed polyesters.

EXPERIMENTAL

Methyl- and phenyl-phosphonic dichlorides were prepared by the procedure described previously [1]. The yields were 70% and 92% respectively. Methylphosphonic dichloride had m.p. 31-32°, and phenylphosphonic dichloride had b.p. 83-84° (1 mm).

Phenyl Phosphorodichloridate. Phenyl phosphorodichloridate was prepared by Jacobsen's method [4] from phenol and phosphoryl chloride. A mixture of 104.5 g (1.1 moles) of phenol and 170.6 g (1.1 moles) of phosphoryl chloride was prepared in a round-bottomed flask fitted with reflux condenser protected by a calcium chloride tube. The mixture was boiled for ten hours. Vacuum fractionation of the reaction mixture gave a fraction of b.p. 97-103° (2 mm) and refractionation gave the acid chloride in 57.7% yield as a colorless liquid; b.p. 103-104° (2 mm); $n^{20}D$ 1.5216; d^{20}_4 1.4145. The literature [4] gives b.p. 241-243° and d^{20}_4 1.4121.

p-Nitrophenyl Phosphorodichloridate. For the reaction we took 139 g (1 mole) of p-nitrophenol and 153.5 g (1 mole) of phosphoryl chloride. The reaction conditions were the same as for the preparation of phenyl phosphorodichloridate. Vacuum fractionation gave a fraction of b.p. 179-180° (3 mm) in 33% yield. The supercooled substance had d^{20}_4 1.5745 and $n^{20}D$ 1.5585.

p-Nitrophenyl phosphorodichloridate is a solid of m.p. 42-43°. The literature [5] gives m.p. 46-48°.

p-Methoxyphenyl Phosphorodichloridate. p-Methoxyphenyl phosphorodichloridate was synthesized by the above-described procedure. For reaction we took 19 g (0.153 mole) of p-methoxyphenol and 23.6 g (0.153 mole) of phosphoryl chloride. Vacuum fractionation gave 20.6 g (55.8%) of a fraction of b.p. 175-176° (5-6 mm); colorless liquid; $n^{20}D$ 1.5335; d^{20}_4 1.4210; found MR 52.67; calculated MR 51.27.

Found %: Cl 29.93; 30.29 $C_7H_7PO_3Cl_2$. Calculated %: Cl 29.46.

p-Methoxyphenol. We synthesized p-methoxyphenol from hydroquinone and dimethyl sulfate [6]; the yield was 26.6 g (43.0% on the amount of hydroquinone taken); b.p. 104-108° (4 mm). After being recrystallized from carbon tetrachloride, the product was obtained as white crystals, m.p. 52-53°, which is in accord with the literature [7]. p-Methoxyphenol is soluble in water, ether, dichloroethane, chloroform, p-xylene, and benzene.

Method of Preparing Polyesters. The polyesters of phosphonic acids of acid phosphoric esters were prepared by condensation of the acid chlorides with hydroquinone in presence of tin (1%). The reaction was carried out in a test tube fitted with side tube and a bubbler for the passage of nitrogen. The reactants were taken in equimolecular proportions. In the condensation, heating in a stream of nitrogen took four hours at 140°, seven hours at 170° one hour at 180°, one hour at 190°, and three hours at 200°. The catalyst (tin) was added to the reaction mixture at 170°.

The authors express their thanks to G. L. Slonimskii for valuable advice and constant interest in the work.

SUMMARY

1. Hydroquinone polyesters of some phosphonic acids and aryl dihydrogen phosphates were synthesized.

2. It was shown that the nature of the group attached to phosphorus has an appreciable effect on the properties of the polyester.

3. Unlike the polymers prepared from aliphatic diols, the analogous polymers with aromatic residues in the main chain are solids.

4. Mixed phosphonic and phosphoric polyesters were prepared. Investigation of the binary systems over the whole gamut of compositions showed that each copolymer has a minimum melting point at a certain composition.

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CARBON-CHAIN POLYMERS AND COPOLYMERS

COMMUNICATION 5. SYNTHESIS AND PROPERTIES OF COPOLYMERS OF ACRYLONITRILE WITH METHYL METHACRYLATE

G. S. Kolesnikov, L. S. Fedorova, B. L. Tsetlin, and N. V. Klimentova

The copolymerization of acrylonitrile with methyl methacrylate has been studied by various investigators [1-9], and the preparation of such copolymers has been the subject of many patents. However, there has been only one systematic investigation of the dependence of the properties of the copolymers on their compositions [3]. In this investigation it was found that the compression strength of copolymers of acrylonitrile with methyl methacrylate depends on composition and is at a maximum when the molar ratio of monomers in the copolymer is 1 : 1. According to patents, copolymerization with acrylonitrile improves the mechanical properties of polymethyl methacrylate. It was noted also that the copolymers are colored.

The present investigation had the object of determining the effect of the proportions of monomers in the original mixture on the composition of the copolymer at relatively high conversions and of studying the dependence of some properties of the copolymers on their composition. The properties of the copolymers which we determined were: intrinsic viscosities as solutions in dimethylformamide at 20°, solubilities in acetone and dichloroethane, and also thermomechanical characteristics, (which enabled us to judge the temperatures of transition into various physical states), temporary resistance to static flexure, and specific resilience.

Polymerization was carried out by the emulsion method and in the mass. In emulsion polymerization we used soap as emulsifier, ammonium persulfate as initiator, and 2-aminoethanol as modifier. On the basis of preliminary experiments the emulsion was prepared according to the following recipe:

Water	200 ml
Soap	2 g
Ammonium persulfate	0.8 g
2-Aminoethanol	0.8 ml
Monomer or mixture of monomers	0.377 mole

Reaction was for five hours at 50°. The copolymers were precipitated from the emulsion by addition of 50 ml of saturated brine containing 1 ml of concentrated sulfuric acid, unchanged monomers were distilled off in steam, and the copolymers were filtered off and washed 3-4 times with distilled water. The copolymers were then boiled with 100-200 ml of methanol for 15 minutes, filtered off, and washed on the filter 2-3 times with hot alcohol; they were then dried to constant weight at 50°.

Mass polymerization was carried out in presence of benzoyl peroxide. The monomer was heated for 72 hours with gradual raising of the temperature from 40° to 120°.

The thermomechanical characteristics were investigated with the aid of curves showing the relation of deformability to temperature. These curves were determined with an apparatus [10] which was a modification of the dynamometric balance [11]; it enabled us to plot the curves by a continuous method, i.e. under conditions of constant loading of the sample throughout the whole experiment. In the measurement of the curves the temperature was caused to rise at a constant rate of 75° per hour. As samples we used emulsion-polymerization powders, which were poured into the cup of the apparatus and given a slight preliminary compacting. The diameter of the compression cylinder was 4 mm, and the load was 500 g. From the thermomechanical curves

we determined the glass point T_g of the polymers, i.e., the temperature at the transition from the glasslike state to the highly elastic state, and the viscous-flow temperature (flow point, T_f), at which the polymer passes from the highly elastic state to the state of viscous flow. In the determination of T_g from the thermomechanical curves, it was conditionally taken to be the temperature at which the deformation attains 5% of the original thickness of the layer of powder under test; T_f was taken to be the temperature at which the curve begins to depart from the straight line corresponding to the highly elastic state of the polymer, and in the absence of such a linear section T_f was taken to be the temperature corresponding to the point of inflection. In the case of mass-polymerization samples, only T_g was determined, and the determination was carried out with a Hoppler consistometer with a constant loading of 2 kg/sq. cm.

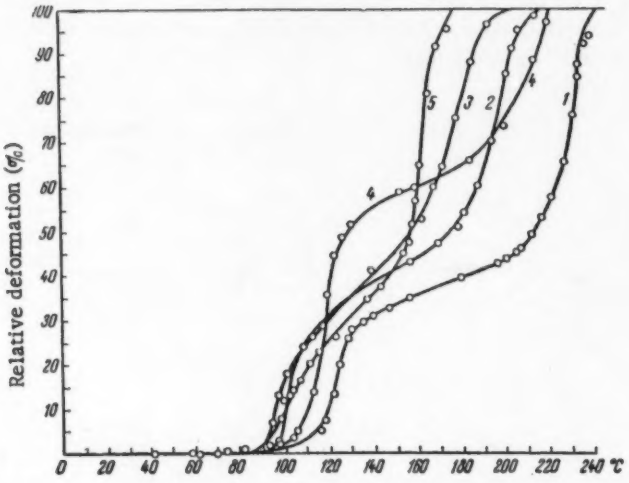

Fig. 1. Thermomechanical curves for the compression of copolymers of acrylonitrile with methyl methacrylate. Content of acrylonitrile in copolymer (moles %): 1) 0.0; 2) 10.6; 3) 19.0; 4) 2.7; 5) 29.0.

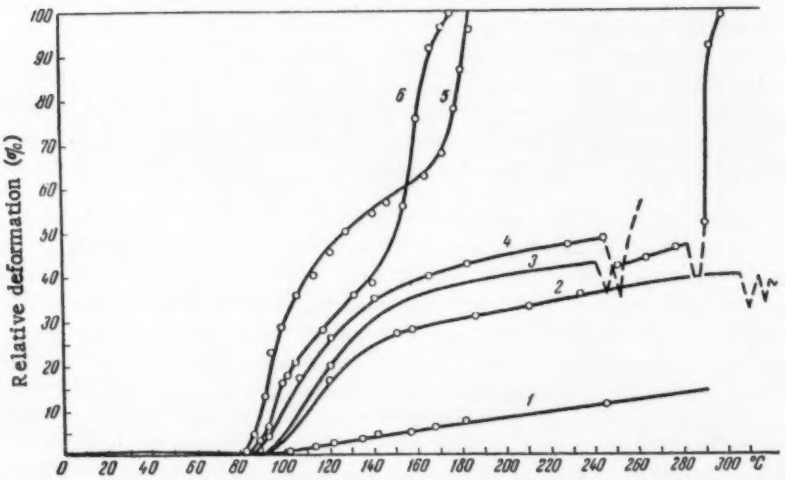

Fig. 2. Thermomechanical curves for the compression of copolymers of acrylonitrile with methyl methacrylate. Content of acrylonitrile in copolymer (moles %) 1) 100; 2) 72.5; 3) 73.0; 4) 62.5; 5) 47.0; 6) 38.2.

Tests on the mechanical strength of the copolymers were carried out on microsamples of size 15 × 10 × 3.5 mm, which were prepared in electrically heated closed compression molds. In most cases the molding temperature corresponded to the viscous-flow state of the polymer and was fixed on the basis of the thermomechanical curves. The samples were tested with a Dynstat pendulum apparatus, with which samples of these dimensions can be tested for the effect of static flexure and impact.

Samples prepared from copolymers containing up to about 40 moles per cent of acrylonitrile were clear and faintly yellow. Copolymers containing 50-60 moles per cent gave brown opaque samples, and from copolymers containing still more acrylonitrile only very weak brittle samples could be prepared. The results obtained in the emulsion copolymerization of acrylonitrile with methyl methacrylate are given in Table 1. They show that methyl methacrylate enters the polymerizing chain more rapidly than acrylonitrile, and the copolymer, in the course of its formation, contains correspondingly more methyl methacrylate residues (relative to acrylonitrile residues) than the original mixture of monomers.

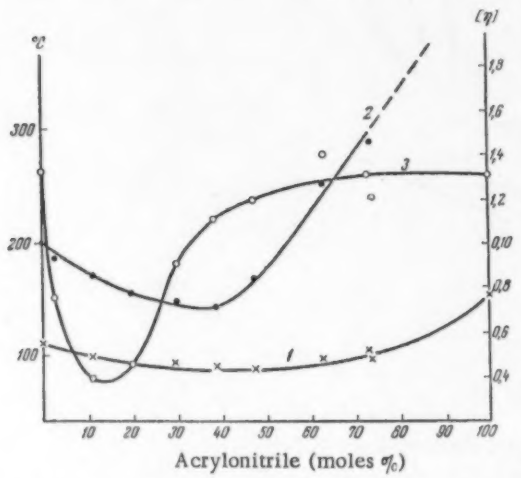

Fig. 3. Relation of T_g (1), T_f (2), and [η] (3) of copolymers to their compositions.

TABLE 1

Emulsion Copolymerization of Acrylonitrile with Methyl Methacrylate

Acrylonitrile content of original mixture (moles %)	Yield of copolymer (%)	Nitrogen content of copolymer (%)	Acrylonitrile content of copolymer (moles %)
100,0	71,5		100,0
80,0	84,0	15,59 15,45	73,0
70,0	86,9	12,41 12,27	64,8
60,0	90,0	7,83 7,81	47,0
50,0	87,0	6,52 6,51	38,2
40,0	83,0	4,55 4,49	29,0
30,0	80,5	2,85 2,90	19,0
20,0	82,5	1,54 1,58	10,6
10,0	82,3	0,38 0,40	2,75
0,0	82,4	—	0,0

The properties of the copolymers are compared in Table 2. The thermomechanical curves of the copolymers are shown in Figures 1 and 2, and Fig. 3 shows the relation of [η] T_g, and T_f of the copolymers to their compositions. It will be seen from Table 2 and Fig. 3 that replacement of a little of the methyl methacrylate of polymethyl methacrylate by acrylonitrile results in a sharp fall in the intrinsic viscosity.

As the acrylonitrile content of the copolymer increases, at first T_g and T_f fall, but after attaining minimum values at an acrylonitrile content of about 40-50 moles per cent they rise again. It is interesting that the minimum values of T_g and T_f, on the one hand, and the minimum values of intrinsic viscosity, on the other, characterize copolymers of different compositions, so that it does not appear to be possible to explain the lowering of T_f solely by the reduction in the molecular weight of the copolymer. It is probable that this lowering, and also the lowering of T_g, is due to the reduction in intermolecular action between copolymer chains resulting from reduction in degree of order. The fact that the copolymers corresponding to the minima on the viscosity and transition-point curves preserve their strength properties (Table 2) indicates that these copolymers have fairly high degrees of polymerization. It is known that copolymers are characterized not only by distribution with respect to molecular weight, but also by distribution with respect to composition; moreover, copolymers differing in composition may be present together and may plasticize each other. It is interesting that T_g is lowered to a greater extent than T_f, and the highly elastic region of the copolymers is accordingly reduced in extent.

TABLE 2

Properties of Copolymers of Acrylonitrile with Methyl Methacrylate

Acrylonitrile content of copolymer (moles %)	[η]	T_g (°C)	T_f (°C)	Solubility • (g/ 100 ml)		Strength	
				in acetone	in $C_2H_4Cl_2$	to static flexure (kg/sq.cm)	Sp. resilience (kg/ cm per sq. cm)
0,0	1,60	112	207	10	10	1070	6,3
2,75	0,75	104	185	10	10	1110	8,5
10,6	0,40	98	171	10	10	1070	5,7
19,0	0,46	92	156	10	10	890	9,6
29,0	0,90	93	148	10	10	820	5,7
38,2	1,10	91	143	10	5		—
47,0	1,16	86	168	1	1	1040	3,5
64,8	1,40	94	254**	1	Swells	580	2,0
72,5	1,27	108	—***	—	»	210	1,5
73,0	1,20	100	290**	—	—	—	
100,0	1,28	155***	—***	—	—	—	—

• The values given for the solubility indicate: 10, that the copolymer forms a 10% solution and can give more concentrated solutions; 5, that the copolymer forms a 5% solution, but cannot give a 10% solution; 1, that the copolymer forms a 1% solution, but does not give a 5% solution.

•• Decomposition occurs simultaneously with flow.

••• The samples decompose without passing into the viscous-flow state.

Table 3 gives results of the investigation of T_g for copolymers prepared by mass copolymerization; in this case the compositions of the copolymers were almost identical with those of the original monomer mixtures. As will be seen from Table 3, copolymers of acrylonitrile with methyl methacrylate prepared by mass polymerization in presence of benzoyl peroxide have glass points in agreement with the values found for emulsion-polymerized products.

TABLE 3

Copolymers of Acrylonitrile with Methyl Methacrylate Prepared by Mass Polymerization

Acrylonitrile content of original mixture (moles %)	Benzoyl peroxide content (moles %)	T_g (°C)	Acrylonitrile content of original mixture (moles %)	Benzoyl peroxide content (moles %)	T_g (°C)
0.0	0.14	1.12	39.9	0.15	91
9.7	0.15	99	50.1	0.14	87
19.8	0.15	95	59.8	0.15	89
30.1	0.15	81	70.1	0.15	84

SUMMARY

1. Copolymers of acrylonitrile with methyl methacrylate were prepared by the emulsion method in high conversions, and their compositions were determined.

2. It was found that minimum intrinsic viscosities of the copolymers, on the one hand, and minimum temperatures of transition into the highly elastic and viscous-flow states, on the other, correspond to copolymers differing in composition.

3. It was shown that copolymers of acrylonitrile with methyl methacrylate containing up to 30 moles per

cent of acrylonitrile have strength characteristics close to those of polymethyl methacrylate.

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BRIEF COMMUNICATIONS

PREPARATION OF ACID BROMIDES OF ORGANOBORON ACIDS FROM ORGANOBORON ESTERS AND ACID CHLORIDES

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When treated with phosphorus pentachloride, organoboron esters are converted smoothly into organoboron acid chlorides of the types: R_2BCl [1, 2], $RBCl_2$ [3, 4], and RBCl (OR) [2, 5]. There naturally arose the question of the possibility of preparing organoboron acid bromides in an analogous way by use of phosphorus pentabromide, instead of the pentachloride.

Unlike phosphorus pentachloride, the pentabromide reacts with isobutyl diphenylborinate only at high temperature. When the mixture is heated in a water bath, reaction is slow; the pentabromide dissolves completely, and the solution becomes dark red as a result of partial dissociation of the pentabromide into bromine and the tribromide. At 130-140° reaction is complete in 30-40 minutes, the completion being indicated by disappearance of the red color. The expected bromodiphenylborine (diphenylborinic bromide), formed by Reaction (1), is obtained only in low yield (16.4%):

$$(C_6H_5)_2BOC_4H_9 + PBr_5 = (C_6H_5)_2\,BBr + C_4H_9Br + POBr_3, \qquad (1)$$

The main product is isobutyl benzenebromoboronate (52%), formed by the simultaneous reaction of the original ester with bromine:

$$PBr_5 = PBr_3 + Br_2; \qquad (2)$$

$$(C_6H_5)_2BOC_4H_9 + Br_2 = C_6H_5BBr(OC_4H_9) + C_6H_5Br \qquad (3)$$

In accordance with Equations (2) and (3), large amounts of bromobenzene and phosphorus tribromide are found in the reaction products.

With the object of reducing the dissociation of phosphorus pentabromide and so creating more favorable conditions for the formation of bromodiphenylborine, we used phosphorus tribromide as solvent in the reaction. Under these conditions the yield of bromodiphenylborine rose to 25.5% and that of the benzenebromoboronic ester was 37.3%. In still higher yield (34%), bromodiphenylborine was prepared by the action of phosphorus pentabromide on ethyl diphenylborinate in a medium of phosphorus tribromide. Bromodiphenylborine was prepared earlier by Michaelis in very low yield and in a contaminated state from diphenylmercury and boron tribromide [6].

At high temperatures diisobutyl benzeneboronate also reacts with phosphorus pentabromide, and is converted in 31.4% yield into the benzenebromoboronic ester in accordance with the following equation

$$C_6H_5B(OC_4H_9)_2 + PBr_5 = C_6H_5\ BBr(OC_4H_9) + POBr_3 + C_4H_9Br \qquad (4)$$

As in the previous case, the reaction is complicated by the dissociation of the phosphorus pentabromide and simultaneous reaction of the ester with bromine with formation of bromobenzene and the bromoboric ester, which decomposes in the subsequent distillation:

$$C_6H_5B(OC_4H_9)_2 + Br_2 = C_6H_5Br + BrB(OC_4H_9)_2 \qquad (5)$$

In this case also the use of phosphorus tribromide has a favorable effect on the course of the process, leading to an increase in the yield of the benzenebromoboronic ester to 41%.

It was found also that organoboron acid bromides are obtained by the action of hydrogen bromide on the corresponding acid chlorides. Passage of hydrogen bromide into chlorodiphenylborine gives a high yield of bromodiphenylborine:

$$(C_6H_5)_2BCl + HBr = (C_6H_5)_2BBr + HCl \quad (6)$$

By the action of hydrogen bromide on dichlorophenylborine we obtained dibromophenylborine (benzeneboronic dibromide):

$$C_6H_5BCl_2 + 2HBr = C_6H_5BBr_2 + 2HCl \quad (7)$$

Isobutyl benzenechloroboronate also reacted with hydrogen bromide and was converted into the benzenebromoboronic ester.

EXPERIMENTAL

Action of Phosphorus Pentabromide on Diphenylborinic Esters

a) In Phosphorus Tribromide. A stirred mixture of isobutyl diphenylborinate (23.8 g; 0.1 mole), phosphorus tribromide (220 g), and phosphorus pentabromide (43 g; 0.1 mole) was heated at 130-140° until the reddish-brown color disappeared (90 minutes). Distillation of the reaction products gave 9 g (37.3%) of isobutyl benzenebromoboronate, b.p. 115-119°,

Found %: B 4.30; Br 32.15 $C_{10}H_{14}OBBr$. Calculated %: B 4.43; Br 33.18.

and 6.4 g (25.5%) of bromodiphenylborine, b.p. 150-153° (8 mm).

Found %: B 4.37; Br 31.70 $C_{12}H_{10}BBr$. Calculated %: B 4.42; Br 32.70.

We obtained also 3.4 g of isobutyl bromide and 4.7 g of bromobenzene.

By the action of phosphorus pentabromide (36.5 g) on ethyl diphenylborinate (18 g; b.p. 137-140° (8 mm)) in phosphorus tribromide (260 g) under the above-described conditions we obtained 7 g (34%) of bromodiphenylborine, b.p. 150-153° (8 mm).

b) Without Solvent. A mixture of 23.8 g of isobutyl diphenylborinate and 43 g of phosphorus pentabromide was heated at 100° until the phosphorus pentabromide dissolved and then at 130-140° for 35 minutes. Distillation of the reaction mixture gave 12.5 g (52%) of isobutyl benzenebromoboronate, b.p. 106-110° (8 mm)and 4 g (16.4%) of bromodiphenylborine, b.p. 150-155° (8 mm). We obtained also 1.9 g of isobutyl bromide, 10.2 g of bromobenzene, 20 g of phosphorus tribromide, and a little phosphoryl bromide.

Action of Phosphorus Pentabromide on Diisobutyl Benzeneboronate

a) In Phosphorus Tribromide. A stirred mixture of 23.4 g (0.1 mole) of diisobutyl benzeneboronate, 240 g of phosphorus tribromide, and 43 g (0.1 mole) of phosphorus tribromide was heated at 100° for 40 minutes and at 120-140° until the dark-red color disappeared (15 minutes). Distillation of the reaction products gave 10 g (41.6%) of isobutyl benzenebromoboronate, b.p. 110-112.5° (9 mm). After being redistilled the substance had: b.p. 112-112.5° (9 mm); d^{20}_4 1.243; $n^{20}D$ 1.5190.

Found %: B 4.63; Br 32.90 $C_{10}H_{14}OBBr$. Calculated %: B 4.43; Br 33.18.

b) Without Solvent. When the reaction was carried out with the same amounts of reactants, but without PBr_3, we obtained 7.5 g (31.4%) of isobutyl benzenebromoboronate, b.p. 98-103° (6.5 mm). In addition we obtained isobutyl bromide, bromobenzene, phosphorus tribromide, and phosphoryl bromide.

Action of Hydrogen Bromide on Chlorodiphenylborine

Dry hydrogen bromide was passed slowly for one hour at room temperature into chlorodiphenylborine (17.3 g; b.p. 131-132.5° (4 mm); [1]; $n^{20}D$ 1.6137),and it was then passed at 0° until the theoretically expected increase in weight had occurred (1 hour). Fractionation gave 15.9 g (75%) of bromodiphenylborine; b.p. 153-154° (9 mm); d^{20}_4 1.302; $n^{20}D$ 1.6325.

Found %: B 4.39, Br 32.24 $C_{12}H_{10}BBr$. Calculated %: B 4.41; Br 32.64.

The literature [6] gives b.p. 150-160° (8 mm).

Action of Hydrogen Bromide on Dichlorophenylborine

Dry hydrogen bromide was passed slowly for six hours at room temperature into dichlorophenylborine (15.2 g; b.p. 57-59° (8 mm) [3]). The increase in weight was about 70% of the expected amount. Fractional distillation gave 6.4 g of unchanged dichlorophenylborine and 3.6 g (34.6%) of dibromophenylborine b.p. 78-82° (7 mm). After being redistilled, the dibromophenylborine had b.p. 78-80° (7 mm), m.p. 31-32°, and d^{30}_4 1.698.

Found %: B 4.47; Br 63.71. $C_6H_5BBr_2$. Calculated %: B 4.43; Br 64.49.

Dibromophenylborine (b.p. 99-101° (20 mm)) was prepared earlier from diphenylmercury and boron tribromide (yield not stated) [7].

All operations were carried out in an atmosphere of nitrogen.

SUMMARY

1. Reaction between phosphorus pentabromide and isobutyl diphenylborinate gives bromodiphenylborine and isobutyl benzenebromoboronate.

2. Reaction between phosphorus pentabromide and diisobutyl benzeneboronate gives isobutyl benzenebromoboronate.

3. The reactions of hydrogen bromide with chlorodiphenylborine and with dichlorophenylborine give bromodiphenylborine and dibromophenylborine respectively.

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DEHYDROGENATION OF HYDROCARBONS OF VARIOUS STRUCTURES IN PRESENCE OF AN ALUMINA–CHROMIA–POTASSIA CATALYST

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It can now be regarded as established that in presence of oxide catalysts under certain conditions, aromatic hydrocarbons are formed both from paraffins having six or more carbon atoms in the main chain, and also from those having less than six carbon atoms in the chain and therefore not capable of direct cyclization [1-5]. In the course of the aromatization of hydrocarbons of various structures a certain amount of unsaturated hydrocarbons is formed. In the study of the aromatization of n-alkanes and isoparaffins attention has been focused mainly on the formation of aromatic hydrocarbons and only to a very much smaller extent on the yields and structures of the unsaturated hydrocarbons. However, the many-sided study of aromatization and dehydrogenation processes, the determination of the relation of the activities of oxide catalysts to the reaction conditions and the structures of the hydrocarbons, and physicochemical investigation of the catalysts will help in the analysis of the mechanisms of these reactions, which are still far from clear, and so enable us to control the course of a given reaction in the desired direction. Some of the isoalkenes containing six or more carbon atoms may find practical application.

In view of these considerations the more detailed investigation of the dehydrogenation of isoparaffins of various structures appears to us to be important. In the present paper we report the first results on the study of the transformations of C_5, C_6, and C_8 hydrocarbons of various structures in presence of an alumina-chromia-potassia catalyst [6]. The work is closely related to our work on the transformation of C_5–C_9 n-alkanes in presence of the same catalyst [7]. After preliminary rectification through a column having an efficiency of 40 theoretical plates, all the hydrocarbons had constants in accord with data in the literature [8]. Branched C_6 paraffins were synthesized by the Grignard method. The experimental conditions were the same as those used for n-alkanes [7]: 500°, space velocity 0.5 hour^{-1}, 30 ml of catalyst, 100 ml of hydrocarbon for each experiment, and duration of experiment 7 hours. After each experiment the catalyst was regenerated with air for 4-5 hours at 700°. Several experiments were carried out under the same conditions. The activity of the catalyst was determined under standard conditions with isopentane and n-hexane, and it was still at its initial level when all the experiments had been carried out (140 hours). The results are presented in the table.

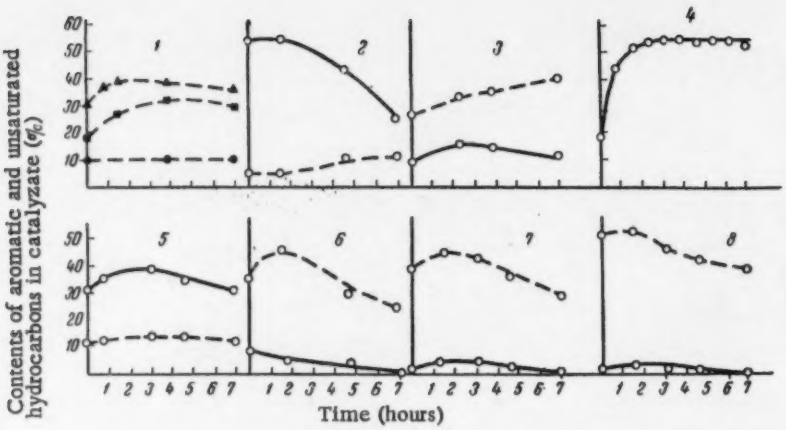
As will be seen, the dehydrogenation of isopentane proceeds further than that of n-pentane. Under the same conditions cyclopentane is dehydrogenated to a much lower extent, with the formation of only 7% of cyclopentane and only about 4% of cyclopentadiene in the catalyzate. Branching in C_6 hydrocarbons favors increase in the yield of unsaturated hydrocarbons and reduction in the yield of aromatics. Under the conditions studied, all the hexane isomers give only 3-4% of aromatic hydrocarbons and 35-46% of unsaturated hydrocarbons (regarded as monoolefins). In view of the high yields of unsaturated hydrocarbons, the dehydrogenation of hexane isomers in presence of an alumina-chromia-potassia catalyst merits careful study in greater detail. We are now investigating the compositions of the unsaturated hydrocarbons formed. Cyclohexane is dehydrogenated to benzene to the extent of 90%. The experiments with C_8 hydrocarbons showed the same general features as those with C_6 hydrocarbons: the aromatics content of the n-octane catalyzate was much greater than that of the isooctane catalyzate (50% and 11%, respectively); there was 8% of unsaturated hydrocarbons in the n-octane catalyzate and 30% in the isooctane catalyzate.

TABLE

Effect of the Structures of Hydrocarbons on the Dehydrogenating and Aromatizing Powers of an Alumina-Chromia-Potassia Catalyst

Hydrocarbon	Yield of catalyzate (%)	n_D^{20}	Iodine value	Content of unsaturated hydrocarbons (%)	Content of diolefins (%)	Relative dispersion	Content of aromatic hydrocarbons (%)	Amount of gas (liters at STP)	Composition of gas		
									H_2	C_nH_{2n}	C_nH_{2n+2}
C_5 hydrocarbons											
n-Pentane	93,5	1,3640	105,4	29,0	Traces	—	Traces	9,048	88,0	0,7	11,3
Isopentane	95,2	1,3655	146,6	38,8	1,3	—	»	10,220	90,8	0,5	8,7
Cyclopentane	87,7	1,4080	41,4	6,7	3,6	—	»	10,950	94,6	2,4	3,0
C_6 hydrocarbons											
n-Hexane	86,6	1,4220	41,5	13,7	—	25,0	42,6	34,400	95,0	0,6	4,4
2-Methylpentane	86,0	1,3830	105,0	34,8	—	20,1	4,2	10,900	85,0	2,9	12,1
3-Methylpentane	88,3	1,3887	119,0	39,7	—	20,2	3,8	12,167	87,4	1,6	11,0
2,3-Dimethylbutane	89,2	1,3875	137,6	45,5	—	20,3	2,5	11,230	90,4	0,6	9,0
Cyclohexane	83,5	1,4900	0,1	Traces	—	—	89,7	57,378	99,0	0,3	0,7
C_8 hydrocarbons											
n-Octane	85,2	1,4502	17,8	7,8	—	25,8	50,2	34,000	92,0	0,2	7,8
2,2,4-Trimethylpentane	80,0	1,3990	67,6	29,8	—	20,5	11,5	11,687	80,3	8,7	11,0

•Calculated as monoolefins.



Relation of yields of unsaturated (------) and aromatic (———) hydrocarbons to the duration of reaction. Original hydrocarbons: 1) △ isopentane, □ n-pentane, ○ cyclopentane; 2) n-octane; 3) isooctane; 4) cyclohexane (the values of the ordinates range from 40 to 100); 5) n-hexane; 6) 2-methylpentane; 7) 3-methylpentane; 8) 2,3-dimethylbutane.

The dependence of aromatics content on the duration of the work of the catalyst is worthy of attention (see figure). Catalyst activity is stable throughout the whole of the experiment only in the case of the dehydrogenation of cyclopentane, and in the other cases catalyst activity changes in various ways with time, depending on the structure of the hydrocarbon and the type of reaction (dehydrogenation or aromatization). An examination of the curve for the dehydrogenation of cyclohexane shows that in the first 2-3 hours the activity of the catalyst rises to a certain level, and in the remaining 4-5 hours it remains almost constant. The curve for the aromatization of n-hexane passes through a maximum; the activity of the catalyst in the last hour is greater than in the first; the content of unsaturated hydrocarbons in the catalyzate remains almost constant (12-14%). The curves for the dehydrogenation of hexane isomers also pass through a maximum. Unlike the case of n-hexane, the aromatics contents of the catalyzates from the hexane isomers falls as the experiment proceeds, and at the end of the experiment they are scarcely formed at all; at this point 2-methylpentane gives 25% of unsaturated hydrocarbons, 3-methylpentane gives 30%, and 2,3-dimethylbutane gives 40%. The curve for the aromatization of n-octane falls, and from the first hour to the last there is a twofold increase in the content of unsaturated hydrocarbons in the catalyzate. The curve for the aromatization of isooctane passes through a maximum, but the content of unsaturated hydrocarbons in the catalyzate increases from 26% at the start of the experiment to 41% at the end. A more detailed investigation of the compositions of the catalyzates from these hydrocarbons will to some extent help in the interpretation of the observed facts.

SUMMARY

1. A study was made of the transformations of C_5, C_6, and C_8 hydrocarbons of various structures in presence of an alumina-chromia-potassia catalyst.

2. Under the given conditions at 500°, from hexane isomers and from isooctane, high yields (30-46% in one passage) of the corresponding unsaturated hydrocarbons were obtained.

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TRANSFORMATIONS OF C_5–C_9 n-ALKANES IN PRESENCE OF AN ALUMINA–CHROMIA–POTASSIA CATALYST

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In investigations, which started in 1936 and are still continuing, on the transformations of C_6 and higher paraffins over oxide catalysts attention has been focused mainly on dehydrocyclization reactions in which aromatic hydrocarbons are formed [1]. In this treatment the dehydrogenation of paraffins has been regarded as an undesirable side reaction. However, the preparation of alkenes, and also alkadienes, by the catalytic dehydrogenation of paraffins is at present of both scientific and practical interest. We therefore decided to determine the possibility of directing the reaction mainly to the formation of alkenes. With this object we investigated the transformations of C_5–C_9 n-alkanes in presence of an alumina-chromia-potassia catalyst, which has been found to have high activity and stability in the dehydrogenation of isopentane [2].

TABLE

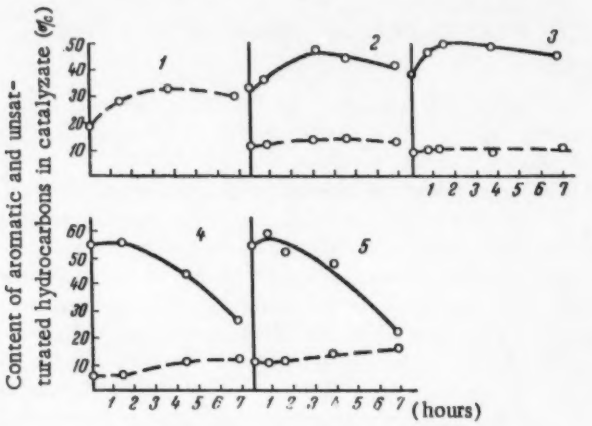
Dehydrogenating and Aromatizing Powers of the Alumina-Chromia-Potassia Catalyst

Hydrocarbon	Yield of catalyzate (%)	n_D^{20}	Iodine value	Relative dispersion	Content of hydrocarbons in catalyzate (%)		Amount of gas (liters at STP)	Composition of gas (%)		
					Unsaturated	Aromatic		H_2	C_nH_{2n}	C_nH_{2n+2}
Pentane	93,5	1,3640	105,4	—	29,0	Traces	9,048	88,0	0,7	11,3
Hexane	86,8	1,4220	41,5	25,0	13,7	42,6	34,400	95,0	0,6	4,4
Heptane	87,9	1,4370	23,6	25,4	9,1	47,0	33,120	92,5	0,5	7,0
Octane	85,2	1,4502	17,8	25,8	7,8	50,2	34,000	92,0	0,2	7,8
Nonane	83,3	1,4460	27,3	24,2	13,5	39,0	29,500	87,5	2,1	10,4

All the original hydrocarbons were carefully rectified through a column of 40-plate efficiency. The constants of the distilled hydrocarbons were in close accord with data in the literature [3]. The experiments were carried out in a flow system at 500°; the hydrocarbons were fed at a space velocity of 0.5 hour^{-1}; in each experiment 100 ml of hydrocarbon was passed over 30 ml of catalyst; the duration of the experiment was 7 hours. Before the experiment 7-8 ml of the hydrocarbon was passed into the system to activate the catalyst and stabilize the temperature. After each experiment the catalyst was regenerated with air at 700° for 4-5 hours. The agreement between duplicate experiments was good. The iodine values of the catalyzates were determined by the bromometric method [4], and the content of aromatic hydrocarbons was determined by the relative-dispersion method [5]. The results are given in the table. It will be seen that the content of unsaturated hydrocarbons in the catalyzate falls with increase in the molecular weight of the original n-alkane in the series pentane–octane, with the exception, however, that a greater amount of unsaturated hydrocarbons is obtained from nonane than from octane (13.5% and 7.8%, respectively). On the other hand, the yield of aromatic hydrocarbons increases with increase in the molecular weight of the original alkane, with the exception, again, that less aromatic hydrocarbons were formed from nonane than from octane (39.0% and 50.2%, respectively).

The table gives the over-all results obtained during 7 hours' work of the catalyst. The figure shows the dependence of the contents of aromatic and unsaturated hydrocarbons in the catalyzates on the duration of reaction

over this period of 7 hours. As will be seen from the figure, the curve for the dehydrogenation of pentane passes through a maximum, the contents of unsaturated hydrocarbons in the hexane and heptane catalyzates remain almost constant throughout the experiments, and in the octane and nonane catalyzates the contents of unsaturated hydrocarbons are 1.5-2 times as high at the end of the experiment as at the beginning. The curves for the aromatization of hexane and heptane pass through a maximum, but at the end of the experiment the activity of the catalyst is still higher than at the beginning. A different picture is observed in the case of octane and nonane. The yields of aromatic hydrocarbons fall sharply as the catalyst continues in work, and their contents in the catalyzates fall by a factor of 2-2.5 in the course of the treatment.



Relation of yields of aromatic (——) and unsaturated (- - - -) hydrocarbons to duration of reaction. Original hydrocarbons: 1) pentane; 2) hexane; 3) heptane; 4) octane; 5) nonane.

As will be seen from the results, we have not yet succeeded in obtaining catalyzates having alkene contents of more than 14% by the dehydrogenation of C_6–C_9 alkanes. However, we consider that by change in catalyst composition and reaction conditions we shall effect a substantial increase in the relative yields of alkenes and aromatic hydrocarbons from n-alkanes.

SUMMARY

1. A study was made of the transformations of C_5–C_9 n-alkanes in presence of an alumina-chromia-potassia catalyst which shows high activity in the dehydrogenation of isopentane.

2. It was shown that, under the given conditions, catalyzates containing 8-29% of unsaturated hydrocarbons and 39-50% of aromatic hydrocarbons are obtained from these alkanes.

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•• Original Russian pagination. See C. B. translation.

STRUCTURE OF THE $Mo(CN)_8^{4-}$ ION

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We have previously [1] deduced analytical expressions and calculated the maximum values of functions and the angles between the directions of maximum values for hybrid atomic orbitals and for various symmetries; the calculations were carried out for coordination numbers from 2 to 9, including 8. It was shown that in the hybridization of d^4sp^3 electrons there may arise seven hybrid orbitals having high maximum values with a symmetry of D_2d (dodecahedron), which corresponds to the configuration found experimentally for the $Mo(CN)_8^{4-}$ ion. A paper by Duculot [2] appeared recently in which analytical expressions for hybrid orbitals are deduced and their maximum values are calculated for coordination number 8. However, on the basis of his analytical expressions Duculot concludes that only relatively weak bonds can arise by the hybridization of d^4sp^3 electrons. Hence, in Duculot's view the experimental fact that such a configuration exists indicates that hybridization occurs not simply with d, p, and s electrons, but with the participation of f electrons, because by the inclusion of f electrons hybrid orbitals having higher maximum values are obtained. This is a rather strange conclusion, for it would scarcely be expected that f electrons would be drawn into bonds with the molybdenum atom (atomic number 42) when it is known that these electrons make their appearance only on the atom of atomic number 58.

We consider that Duculot came to this conclusion as a result of his method of constructing hybrid orbitals, which, in our opinion, is arbitrary and unsound and can lead to incorrect values of the maxima of hybrid functions.

Duculot makes the linear combinations of hybrid functions equal to atomic s, p, d, and f orbitals of the same symmetry. By the use of only d^4sp^3 orbitals two sets of four of nonequivalent hybrid orbitals arise. Four hybrid functions have the maximum value 2.512, and the other four should give weak bonds (maximum value 1.483) because they are disposed in the xy plane and the inclusion of d_{z^2} orbitals in the hybridization cannot, of course, lead to strong hybrid bonds. Duculot, therefore, seeks a second set of hybrid orbitals in which the atomic orbital d_{z^2} is replaced by f_{xyz}; moreover, instead of the p_x and p_y orbitals, linear combinations with f orbitals of the form $0.675p \pm 0.737f$ are taken. Hence, altogether three d, one s, three p, and three f electrons are drawn into the hybridization. This, of course, enables us to make sure that hybrid orbitals having maximum values can be formed, but the possibility of forming stable orbitals can scarcely serve as an argument in favor of the orbitals obtained by Duculot, for the inclusion of a still greater number of d and f electrons will probably allow us to obtain still more stable orbitals. If we confine ourselves merely to the replacement of the d_{z^2} orbital by f_{xyz}, then there will be no considerable increase in the strength of the hybrid bonds.

We consider that in the construction of hybrid orbitals it is necessary to start from a number of atomic functions corresponding to the number of hybrid orbitals, but hybrid orbitals must be made equal, not to separate atomic functions, but to linear combinations of atomic orbitals of the same symmetry (e.g. hybrid orbitals of symmetry A_1 must be made equal to linear combinations of atomic orbitals of the same symmetry, $s + d_{z^2}$ and $s - d_{z^2}$). In this treatment the function d_{z^2} is found to be included not only in the hybrid orbitals in the xy plane, but also in the orbitals in the xz plane, the stability of which it may raise greatly. In this scheme, which we believe corresponds to actuality, we find 8 hybrid orbitals corresponding to the configuration D_2d and having fairly high maximum values (2.917 for one set of four and 2.884 for the other), which ensures adequate bond strengths in the $Mo(CN)_8^{4-}$ ion without the introduction of f electrons.

SUMMARY

The question of the hybridization of the atomic orbitals of Mo in the $Mo(CN)_8^{4-}$ ion is examined, and it is shown that the dodecahedral structure can exist without the participation of f electrons.

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SYNTHESIS OF DIETHOXYMETHYL[m-(TRIFLUOROMETHYL)PHENYL]SILANE AND TRIETHOXY[m-(TRIFLUOROMETHYL)PHENYL]SILANE

Ia. I. Mindlin and K. A. Andrianov

Papers have appeared recently in ever-growing numbers on the synthesis of monomeric and polymeric organosilicon compounds having functional groups in silicon-attached alkyl and aryl groups. The present paper is devoted to the synthesis of ethoxyphenyl- and ethoxymethylphenylsilanes having trifluoromethyl in the phenyl group. The synthesis of such compounds is of considerable interest, for it is known that the CF_3 group increases the stability of the phenyl group to thermal oxidation. There are references in the literature to the enhanced chemical stability of organosilicon compounds containing the trifluoromethyl group [1, 2].

To synthesize these compounds we prepared benzotrifluoride by the exchange reaction between benzotrichloride and antimony trifluoride in presence of antimony pentachloride. Benzotrifluoride was brominated with bromine in presence of iron filings with formation of m-bromobenzotrifluoride in 53% yield. The final products were synthesized in one stage by the reaction of magnesium with a mixture of $m\text{-}BrC_6H_4CF_3$ and $Si(OC_2H_5)_4$ or $CH_3Si(OC_2H_5)_3$.

The synthesis can be represented by the following reaction schemes:

1. $C_6H_5CCl_3 + SbF_3 \xrightarrow{Sb^{+5}} C_6H_5CF_3$.

2. $C_6H_5CF_3 + Br_2 \xrightarrow{Fe} m\text{-}BrC_6H_4CF_3$.

3. $m\text{-}BrC_6H_4CF_3 + Mg + CH_3Si(OC_2H_5)_3$ [or $Si(OC_2H_5)_4$] $\rightarrow$ $m\text{-}CF_3C_6H_4Si(CH_3)(OC_2H_5)_4$ / $m\text{-}CF_3H_4Si(OC_2H_5)_3$.

EXPERIMENTAL

Synthesis of Benzotrifluoride. A mixture of 500 g (2.5 moles) of benzotrichloride, 250 g (1.4 moles) of antimony trifluoride, and 12.5 g. (2% on the weight of SbF_3) of antimony pentafluoride was prepared in a one-liter horizontal autoclave. The autoclave was heated to 140°. The duration of reaction was 3-3.5 hours. The maximum pressure was 30-35 atm. After the reaction the product was distilled from the autoclave, washed until neutral, dried over calcined sodium sulfate, and fractionated at ordinary pressure. We obtained Fraction I, b.p. 102-103°; 185 g (55%, calculated on $CCl_3C_6H_5$); $n^{20}D$ 1.4155; d^{20}_4 1.193; found MR 30.65; calculated for $CF_3C_6H_5$ MR 30.65; and Fraction II, b.p. 138-142°; 35 g.

Synthesis of m-Bromobenzotrifluoride. A mixture of 133 g (0.91 mole) of benzotrifluoride and 1 g of iron filings was prepared in a one-liter three-necked flask and heated to 60° in a water bath; 3 ml of dry bromine was added. When the reaction stopped the bath temperature was raised to 70° and a further 1 g of iron filings was added. Bromine (21 ml) was then added at 56-60° over a period of one hour. In the course of the following hour a further 25 ml of bromine was added at the same temperature. When the liberation of hydrogen bromide ceased the contents of the flask were poured into 700 ml of water. To remove excess of bromine the reaction

mixture was treated with sulfur dioxide, washed with water until neutral, and steam-distilled. The oily layer of m-bromobenzotrifluoride was separated from water and dried over sodium sulfate. Fractionation at atmospheric pressure gave Fraction I, b.p. 110-150°, 27 g (mixture of $C_6H_5CF_3$ and $m\text{-}BrC_6H_4CF_3$); Fraction II, b.p. 150-151°, 108 g ($m\text{-}BrC_6H_4CF_3$), yield 53%; $n^{20}D$ 1.4710; d^{20}_4 1.613; found MR 39.36; calculated for $m\text{-}BrC_6H_4CF_3$ MR 39.381.

Synthesis of Diethoxymethyl[m-(trifluoromethyl)phenyl]silane. Magnesium turnings (25 g) were introduced into a one-liter three-necked flask, moistened with 10-15 ml of ether, and heated to 70-80°. The temperature was then lowered to 60°, and a mixture of 178 g (1 mole) of $CH_3Si(OC_2H_5)_3$ and 217.3 g (1.25 moles) $m\text{-}BrC_6H_4CF_3$ was added from a dropping funnel. The reaction went with slight evolution of heat. When the whole of the mixture had been added, the contents of the flask were heated at 70-80° for two hours. The liquid reaction products were distilled from the precipitate at a residual pressure of 10-15 mm and a bath temperature of not above 120°. The distillate was redistilled at a residual pressure of 13 mm, and this gave Fraction I, b.p. 20-40° (13 mm), 140 g (a mixture of $CH_3Si(OC_2H_5)_3$ and $m\text{-}BrC_6H_4CF_3$), and Fraction II, b.p. 105-108° (13 mm), 82.9 g (30%), d^{20}_4 1.081 ($CF_3C_6H_4Si(OC_2H_5)_2$, with CH_3 on Si).

Analysis of Fraction II

Found %: (OC_2H_5) 32.1; SiO_2 21.25. Calculated %: (OC_2H_5) 32.4; SiO_2 21.6.

Synthesis of Triethoxy[m-(trifluoromethyl)phenyl]silane. Magnesium turnings (25 g) were introduced into a one-liter three-necked flask. The magnesium was moistened with 10-15 ml of ether and was heated to 70-80°. A mixture of 271.2 g (1.25 moles) of $m\text{-}BrC_6H_4CF_3$ and 208 g (1 mole) of $Si(OC_2H_5)_4$ was added from a dropping funnel at a bath temperature of 60°. Reaction began after about 10-15 minutes; the synthesis took 2.5-3 hours.

The liquid reaction products were distilled from the precipitate at a residual pressure of 10-12 mm and a bath temperature of up to 120°. The liquid distillate was redistilled at atmospheric pressure and gave Fraction I, b.p. 150-198°, 20 g (a mixture of $Si(OC_2H_5)_4$ and $m\text{-}BrC_6H_4CF_3$), and Fraction II, 124.1 g ($m\text{-}CF_3C_6H_4Si(OC_2H_5)_3$), a clear colorless liquid; d^{20}_4 1.12. There was a crystalline residue (57 g).

Analysis of Fraction II

Found %: (OC_2H_5) 43.9; SiO_2 19.3 $m\text{-}CF_3C_6H_4Si(OC_2H_5)_3$. Calculated %: (OC_2H_5) 44; SiO_2 19.5.

SUMMARY

Diethoxymethyl[m-(trifluoromethyl)phenyl]silane and triethoxy[m-(trifluoromethyl)phenyl]silane were synthesized.

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PREPARATION OF N-OXIDES OF α- AND α'-AMINONICOTINES

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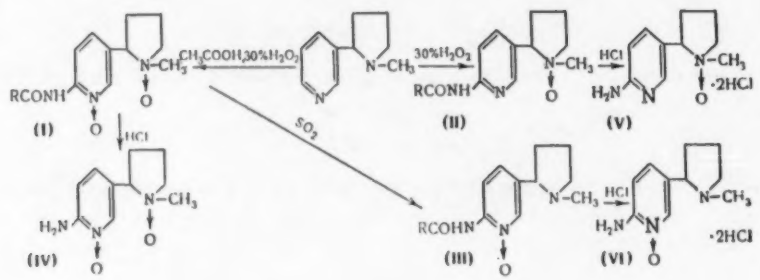
In previous communications we have described the N-oxides of nicotine [1] and of N-methylanabasine [2]. As subjects for further investigations in this field we selected amino- and (acylamino)-nicotines, because these are already of interest as physiologically active compounds [3]. The work was carried out mainly with derivatives of α'-benzamidonicotine. All possible N-oxides of α'-benzamidonicotine, (I), (II), and (III), were prepared, and by hydrolyzing them with hydrochloric acid we obtained the hydrochlorides of N-oxides of α'-aminonicotine (IV), (V), and (VI).

Like the 1-oxides of 2-amino- and 2-(acylamino)-pyridines described by Adams and Miyano [4] and Katritzky [5], the Pl, Py-dioxide and Py-monoxide give colorations with ferric chloride: the amines blue and their benzoyl derivatives red. The Pl-monoxide does not give a color with ferric chloride. All three N-oxides of α'-benzamidonicotine are amphoteric compounds, soluble in caustic alkalis and in mineral acids. At present we consider the formulas (I), (II), and (III) which we give for the N-oxides of α'-benzamidonicotine to be tentative, for the possibility that under certain conditions (I) and (III) may exist as 1,2,4-oxadiazoles cannot be excluded. We hope to clarify this matter in the future.



EXPERIMENTAL

1. Pl,Py-Dioxide of α'-Benzamidonicotine (I) (Monohydrochloride). Glacial Acetic acid (150 ml) and 30% H_2O_2 (35 ml) were added to 12 g of α'-benzamidonicotine, and the solution was heated for six hours at 65-70°. The light-yellow oil obtained after removal of solvent by distillation and suitable treatment with water and alcohol was dissolved in 50% alcohol, and the solution was acidified to Congo red with concentrated hydrochloric acid. The precipitate was filtered off, crystallized twice from alcohol, washed with ether, and vacuum-dried at 80°. We obtained 8.5 g (about 55%) of the hydrochloride, m.p. 197-198° (colorless rhombic plates). It gave a red color with $FeCl_3$.

Found %: C 56.83; H 5.81; N 11.71; Cl 9.71 $C_{17}H_{20}O_3N_3Cl \cdot {}^1/_2H_2O$. Calculated %: C 56.91; H 5.86; N 11.71; Cl 9.90.

The residue after vacuum distillation of the filtrate was hydrolyzed with 12% hydrochloric acid. This gave 2.05 g of benzoic acid and 2.7 g of the dihydrochloride of the Pl,Py-dioxide of α'-aminonicotine, m.p. 190-191° (recrystallized twice from alcohol). With ferric chloride it gave a dark-blue color.

2. Base of Pl, Py-Dioxide of α'-Benzamidonicotine. Alcoholic NaOH was added to 1.8 g of the hydrochloride until the pH attained the value of 6. Alcohol was distilled off under reduced pressure, and the residue was treated with chloroform. After removal of solvent we obtained 1.3 g of yellow crystals, m.p. 116-117° (vacuum-dried at 60°).

Found %: C 55.83; H 6.80; N 11.63 $C_{17}H_{19}O_3N_3 \cdot 3H_2O$. Calculated %: C 55.59; H 6.84; N 11.44.

Vacuum drying at 110° (1.5 mm) gave an amorphous substance which decomposed at 159-162°.

Found %: C 64.33; H 6.01. $C_{17}H_{19}O_3N_3$. Calculated %: C 64.85; H 6.07.

The monopicrate formed yellow needles from water, m.p. 225°.

Found %: N 15.82. $C_{23}H_{22}O_{10}N_6$. Calculated %: N 15.50.

The perchlorate formed colorless needles from methanol, m.p. 222°.

Found %: C 49.47; H 4.86. $C_{17}H_{20}O_7N_3Cl$. Calculated %: C 49.39; H 4.84.

3. Pl, Py-Dioxide of α'-Aminonicotine (Dihydrochloride of (IV)). The dihydrochloride of (IV) was prepared by the hydrolysis of 5 g of the benzoyl derivative (I) with 12% hydrochloric acid. We isolated 1.42 g of benzoic acid and 3.56 g of the dihydrochloride of (IV), m.p. 191-192°. Vacuum drying at 100° raised the m.p. to 197-198°.

Found %: C 39.71; H 6.16; N 13.79; Cl 23.58. $C_{10}H_{17}O_2N_3Cl_2 \cdot H_2O$. Calculated %: C 40.00; H 6.33; N 14.00; Cl 23.66.

In a mixture test there was no depression of melting point with the product of Experiment 1.

The dipicrate formed yellow needles from water; m.p. 212-213°.

Found %: C 39.56; H 2.96; N 18.46. $C_{22}H_{21}O_{16}N_9$. Calculated %: C 39.73; H 3.13; N 18.88.

4. Base of the Pl,Py-Dioxide of α'-Aminonicotine. This was prepared by decomposition of the dihydrochloride of (IV) with saturated potassium carbonate solution, extraction with isobutyl alcohol, and recrystallization from alcohol-ether. From 3 g we obtained 1.87 g of the dioxide, m.p. 198-200° (vacuum-dried at 100°). It gave a dark-blue color with ferric chloride.

Found %: C 52.83; H 7.51; N 18.72. $C_{10}H_{15}O_2N_3H_2O$. Calculated %: C 52.63; H 7.46; N 18.42.

5. Py-Oxide of α'-Benzamidonicotine (III). A cooled solution of 2 g of the Pl,Py-dioxide of α'-benzamidonicotine in 50 ml of absolute alcohol was saturated with sulfur dioxide and then left overnight at room temperature. Excess of SO_2 was removed in a stream of cold air, solvent was distilled off under reduced pressure, and the residue was treated with saturated potassium carbonate solution, extracted with chloroform, and dried with potassium carbonate. The product obtained after removal of solvent was treated with boiling ether. The ether was partially distilled off, and we obtained 1.14 g of a white crystalline substance, m.p. 127-128°. It gave a red color with ferric chloride.

Found %: C 68.29; H 6.34; N 14.04. $C_{17}H_{19}O_2N_3$. Calculated %: C 68.58; H 6.39; N 14.14.

The monopicrate had m.p. 209° (from water).

Found %: N 16.13 $C_{23}H_{22}O_9N_6$. Calculated %: N 15.97.

6. Py-Oxide of α'-Aminonicotine (the Dihydrochloride (VI)). The Py-oxide of α'-benzamidonicotine (III) (0.5 g) was heated for two hours with 12% hydrochloric acid, solvent was distilled off under reduced pressure, benzoic acid was separated, and we obtained a solid hydrochloride. Recrystallization of this from alcohol-ether gave 0.31 g of the dihydrochloride (prismatic needles), m.p. 137-139°. It gave a dark-blue color with ferric chloride.

Found %: C 39.34; H 6.94; Cl 22.87. $C_{10}H_{17}ON_3Cl_2 \cdot 2H_2O$. Calculated %: C 39.74; H 6.95; Cl 23.17.

7. Pl-Oxide of α'-Benzamidonicotine (II). α'-Benzamidonicotine (5 g) was heated for one hour with 8 ml of 30% H_2O_2 in a boiling water bath. Water (50 ml) was added to the mixture, and solvent was distilled off under reduced pressure. This treatment was repeated twice with water and twice with absolute alcohol. The

residue was recrystallized from methanol-acetone. We obtained 3.7 g of a white crystalline substance, m.p. 208-209° (after being dried under reduced pressure at 100°); it gave no color with ferric chloride.

Found %: C 68.24; H 6.58; N 14.04 $C_{17}H_{19}O_2N_3$. Calculated %: C 68.68; H 6.39; N 14.14.

The monopicrate formed yellow needles from methanol; m.p. 207°.

Found %: N 16.16. $C_{23}H_{22}O_9N_6$. Calculated %: N 15.97.

8. Pl-Oxide of α'-Aminonicotine (the Dihydrochloride (V)). This was prepared by the hydrolysis of (II) with 12% hydrocloric acid. Solvent was distilled off, and after being recrystallized from alcohol-ether the hydrochloride had m.p. 150-153° (with decomposition).

Found %: C 45.80; H 6.42. $C_{10}H_{17}ON_3Cl_2$. Calculated %: C 45.11; H 6.32.

The dipicrate formed yellow needles from water; m.p. 241°.

Found %: N 19.95 $C_{22}H_{21}O_{15}N_9$. Calculated %: N 19.35

9. Pl,Py-Dioxide of α-Aminonicotine (Dihydrochloride). α-Benzamidonicotine (3 g)was heated for six hours at 67-70° with 30 ml of glacial acetic acid and 5 ml of H_2O_2. The residue remaining after the removal of solvent was treated as in Experiment 1. The product was a mixture of the Pl, Py-dioxide of α-benzamidonicotine and the Pl,Py-dioxide of α -aminonicotine; it gave a bluish-lilac color with $FeCl_3$. Benzoic acid (0.58 g) was extracted with ether. The oxidation product was hydrolyzed with 12% hydrochloric acid, the acid was removed by distillation, and the residue was crystallized from alcohol-ether. The product (0.91 g) was very hygroscopic. After being vacuum-dried at 80° (1.5 mm), the hydrochloride melted with decomposition at 160-162° (partial fusion at 128°); it gave a blue color with ferric chloride.

Found %: C 40.07; H 6.45; Cl 23.33 $C_{10}H_{17}O_2N_3Cl_2 \cdot H_2O$. Calculated %: C 40.00; H 6.33; Cl 23.66.

The dipicrate formed yellow needles from water; m.p. 197°.

Found %: N 19.16 $C_{22}H_{21}O_{16}N_9$. Calculated %: N 18.88.

SUMMARY

All possible N-oxides of α'-benzamidonicotine were prepared and were hydrolyzed with hydrochloric acid to N-oxides of the corresponding α'-aminonicotines.

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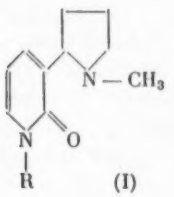
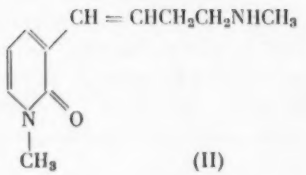
Py-METHYL-α-METANICOTONE. ACTION OF BENZOYL CHLORIDE ON Py-METHYL-α-NICOTONE •

Ia. L. Gol'dfarb and V. V. Kiseleva

As a result of the investigation of a series of derivatives of nicotine and metanicotine[1-4] it was found that these bases, while being less toxic than nicotine, preserve some of its useful pharmacological properties. On the other hand, Karrer and co-workers [5] showed that Py-alkylnicotones of structure (I), which they synthesized, are also less toxic than nicotine, but no longer retain its characteristic property of increasing blood pressure. In this connection it was considered to be of interest to prepare an isomer of (I, R =CH_3), namely Py-methyl-α-nicotone (II), which contains an aminoalkenyl residue instead of the pyrrolidine ring, and to compare its phamacological properties with those of the corresponding substituted α-pyridonimine of structure (III) [3].



(I)



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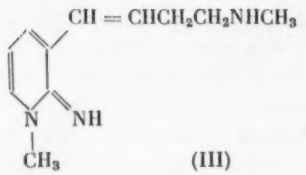
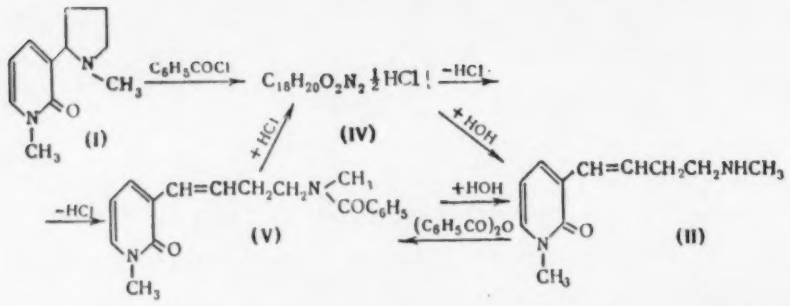


(III)

As starting material for the preparation of the base (II) we used Py-methylnicotone (I, R = CH_3), which was described by Karrer [5]. For the cleavage of the pyrrolidine ring we used Pinner's method [6,7], which consists in the action of benzoyl chloride or acetic anhydride. Our experiments showed that, even under the relatively mild conditions described by Spath and Bobenberger [8], reaction with Py-methylnicotone (I) is accompanied by considerable resinification. After several experiments we succeeded in showing that the cleavage of the pyrrolidine ring proceeds fairly smoothly when Py-methylnicotone (I) is heated with benzoyl chloride in benzene solution. Under these conditions the reaction product is precipitated in the crystalline state. After purification we isolated a substance of m.p. 163.5-164.5° having elementary composition $C_{18}H_{20}N_2O_2 \cdot {}^1/_2$ HCl (IV), which did not correspond to the product of the addition of benzoyl chloride to nicotone analogous to the product isolated by Pinner [6, 7] and later by Loffler and Kober [9] in the reaction with nicotine. The aqueous solution of (IV) was made alkaline, and by extraction with chloroform we isolated 1-methyl-3-[4(N--methylbenzamido)-1-butenyl]-2(1H)-pyridone (V), which again gave the compound (IV) when treated with HCl. Study of the properties of (IV) led us to the conclusion that it is probably the half-hydrochloride of 1-methyl--3-[4-(N-methylbenzamido)-1-butenyl]-2(1H)-pyridone. When boiled with hydrochloric acid, both (IV) and (V) gave the base (II).

It is interesting that the benzoyl derivative (V) gives a crystalline picrate in which there are two molecules of (V) per molecule of picric acid, but treatment with perchloric acid gives a salt containing one molecule of (V) per molecule of acid. With picric acid in alcoholic solution, the base (II) forms a monopicrate, and with HCl it forms a dihydrochloride. The question of the possible causes of the differences in compositions of the salts of these bases will be the subject of future work.

•Py denotes pyridine N. — Publisher.



EXPERIMENTAL

Py-Methylnicotone was prepared by Karrer's method [5] by the oxidation of the hydriodide of the Py-methiodide of nicotine with potassium ferricyanide, but we modified the method of extracting it from the reaction mixture, mainly with the object of isolating unchanged reactant. After the salting-out with potassium carbonate, the solution was extracted with chloroform, chloroform was distilled off, and the oily residue was treated with benzene; the Py-methylnicotone then passed into solution, and the Py-methiodide of nicotone (as the base) remained in a fairly pure state (yield 43%) and could be used again in the oxidation. After removal of benzene and vacuum distillation of the residue we obtained Py-methylnicotone in 30-35% yield (Karrer's yield was 18%).

Action of Benzoyl Chloride on Py-Methyl-α-nicotone. A solution of 3.3 ml of benzoyl chloride in 5 ml of dry benzene was added gradually to a solution of 5 g of Py-methylnicotone (m.p. 85°) in 25 ml of dry benzene; an oil separated at the bottom of the flask. The mixture was heated for five hours in a water bath; the oil crystallized. The clear solution was decanted, and the residue was ground up several times with benzene and then with ether to purify it from benzoyl chloride. The dried product (7.9 g, 97%) melted at 152-155°. Crystallization from alcohol gave 5.6 g (70%) of colorless crystals, m.p. 162-164°, raised by recrystallization to 163.5-164.5°. The substance is soluble in hot water and alcohol, and is insoluble in ether and dioxane; it decolorizes permanganate solution and bromine water. Spectrographic investigations confirmed the presence of a double bond conjugated with the double bonds of the pyridine ring.

Found %: C 68.47; H 6.67; N 8.79; Cl 5.93; HCl 5.78 $C_{18}H_{20}O_2N_2 \cdot \frac{1}{2}$ HCl. Calculated %: C 68.74; H 6.52; N 8.91; Cl 5.65; HCl 5.8

The HCl content was determined by titration of an aqueous solution with 0.01 N NaOH to Bromocresol purple. When the substance (IV) was heated with alcoholic HCl, no change occurred, i.e. there was no addition of HCl.

Preparation of 1-Methyl-3-[4-(N-methylbenzamido)-1-butenyl]-2(1H)-pyridone. A product of m.p. 160-162° was prepared from 20 g of Py-methylnicotone and 13.2 ml of benzoyl chloride under the conditions described for the preceding experiment. Without purification, it was dissolved in 150 ml of 10% hydrochloric acid by warming slightly, and the solution was extracted several times with ether to purify it from benzoic acid; with cooling, it was then made definitely alkaline [8]. The oil that separated was extracted with chloroform. The dark-red oil which remained after removal of chloroform was crystallized under a layer of ether. This gave 26 g of a substance of m.p. 88-92°. Recrystallization from benzene gave 21.2 g (70%), m.p. 96-98°, raised to 99.5-101° by further recrystallization (needles from benzene). 1-Methyl-3-[4-(N-methylbenzamido)-1--butenyl]-2(1H)-pyridone is readily soluble in water, alcohol, and hot benzene, but is sparingly soluble in hot ether.

Found %: C 72.99; H 6.93; N 9.20 $C_{18}H_{20}N_2O_2$. Calculated %: C 72.97; H 6.76; N 9.46.

The perchlorate had m.p. 214-215° (from water).

Found %: C 54.78; H 5.47; Cl 8.69 $C_{18}H_{21}O_6N_2Cl$. Calculated %: C 54.47; H 5.30; Cl 8.95.

The same perchlorate is formed by the addition of perchloric acid to an alcoholic solution of (II).

The picrate had m.p. 133-134° (from water).

Found %: C 61.06; H 5.16; N 11.93 $C_{18}H_{20}N_2O_2 \cdot {}^1/_2\ C_6H_3N_3O_7$. Calculated %: C 61.39; H 5.24; N 11.94.

When 0.5 g of (V) was heated with 0.3 ml of a 10% solution of HCl in absolute methanol (0.5 mole of HCl per mole of (V)), (IV) was obtained in 86% yield. The same substance was obtained when (V) was heated with hydrogen chloride (1 mole per mole of (V)).

Hydrolysis of (IV). Boiling of 20 g of (IV) with 1 : 1 hydrochloric acid for ten hours gave 7.5 g (92%) of benzoic acid and 16.6 g (92%) of the dihydrochloride of 1-methyl-3-(4-methylamino-1-butenyl)-2(1H)--pyridone, m.p. 213-214°. Two recrystallizations from absolute alcohol gave crystals of m.p. 226-227° (in a sealed capillary).

Found %: C 49.66; H 6.87; Cl 26.16 $C_{11}H_{16}N_2O \cdot 2HCl$. Calculated %: C 49.81; H 6.80; Cl 26.79.

The base of 1-methyl-3-(4-methylamino-1-butenyl)-2(1H)-pyridone was isolated in the usual way from the dihydrochloride as a light-yellow oil, which was twice redistilled under reduced pressure; b.p. 180° (2mm) and 174° (1.5 mm).

Found %: C 68.72; H 8.27 $C_{11}H_{16}N_2O$. Calculated %: C 68.75; H 8.33.

The equivalent weight of the substance was determined by titration of a weighed amount with 0.1 N H_2SO_4 to Bromothymol blue; values found were 198, 199, and 198; calculated M 192.

After the addition of alcoholic HCl to an alcoholic solution of the base, the hydrochloride was precipitated with ether; it was found to be identical with the original dihydrochloride of 1-methyl-3-(4-methylamino-1--butenyl)-2(1H)-pyridone. The same dihydrochloride was obtained from the base isolated after the hydrolysis of (V). By benzoylation of the base with benzoyl anhydride in benzene, the benzoyl derivative (V) was obtained in 97% yield.

Monopicrate of the base: m.p. 231-233° (orange needles from alcohol); m.p. 233-235° (from water).

Found %: N 16.44 $C_{17}H_{19}N_5O_8$. Calculated %: N 16.63.

The same monopicrate was prepared from the base isolated after the hydrolysis of (V).

SUMMARY

1-Methyl-3-[4-(N-methylbenzamido)-1-butenyl]-2(1H)-pyridone was prepared by cleavage of the pyrrolidine ring of Py-methyl-α-nicotone with benzoyl chloride, and hydrolysis of this product gave Py-methyl-α--metanicotone.

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LETTERS TO THE EDITOR

MECHANISM OF THE POLYMERIZATION OF ACRYLONITRILE IN PRESENCE OF TRIBUTYLBORINE

Alkylborines constitute a new type of catalyst for the polymerization of unsaturated compounds [1-5], and the elucidation of the mechanism of their catalytic action is of undoubted interest. In a study of the emulsion polymerization of acrylonitrile in presence of tributylborine we showed that in absence of oxygen (both in the liquid and gas phases) acrylonitrile does not polymerize at 20° and 50°. On the other hand, when the acrylonitrile or water (or both of these) are not freed from oxygen, or the polymerization is carried out without displacement of air from the ampoule with nitrogen, the polymerization of acrylonitrile proceeds readily and the yield of polyacrylonitrile attains 60%. It is probable that the initiation of the polymerization of acrylonitrile with tributylborine includes an intermediate stage of formation of products of reaction between tributylborine and oxygen, which are the actual initiators of the polymerization. These products may be peroxy compounds; it is known that trimethylborine readily forms a peroxide when treated with oxygen [6].

The low yield of polyacrylonitrile which we obtained [1] in the polymerization of acrylonitrile in presence of tributylborine in toluene is to be explained by the fact that the polymerization was carried out in an atmosphere of oxygen-free nitrogen and the solvent and monomer were distilled before the polymerization, so that they were freed from most of the dissolved oxygen.

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CATALYTIC HYDROGENATION OF FLUORO OLEFINS

We consider that study of the catalytic hydrogenation of fluoro olefins is not only of practical importance, but has a direct bearing on the important question of the theory of heterogeneous catalysis. The rate of hydrogenation should be dependent on the state of the π-bond of the olefin and should increase with reduction in its electron density if the first act is the removal of electrons by the olefin molecule from the lattice of the catalyst. In this respect, fluoro olefins, which have an exceptionally high affinity for nucleophiles, are unique compounds. We showed that fully fluorinated ethylene, propene, isobutene, and other olefins are smoothly hydrogenated by molecular hydrogen over palladium and nickel catalysts.

TABLE

Original olefin	Catalyst	Hydrogenation temperature (°C)	Hydrogenation product	Yield (%)	B.p. (°C)
$CF_2=CF_2$	Pd	~20	CF_2HCF_2H	96	—22,5
$CF_2=CF_2$	Ni	90—100	CF_2HCF_2H	66	—22,5
			CF_2HCFH_2	14	3
$CF_3CF=CF_2$	Pd	~20	CF_3CFHCF_2H (I)	96	5
$(CF_3)_2C=CF_2$	Pd	~20	$(CF_3)_2CHCF_2H$ (II)	95	33
$(CF_3)_2C=CF_2$	Ni	100	$(CF_3)_2CHCF_2H$	10	33
			$(CF_3)_2CHCH_3$	75	21
$CF_2=CFCl$	Pd	~20	$CF_2=CFH$	60	—51
			CF_2HCFH_2	25	3
$CF_3—CF=CFH$ (IV)	Pd	~20	$CF_3CFH—CFH_2$	65	20
$(CF_3)_2C=CFH$ (V)	Pd	~20	$(CF_3)_2CHCFH_2$ (III)	85	40
$(CF_3)_2C=CH_2$ (VI)	Pd	~20	$(CF_3)_2CHCH_3$	85	21

The hydrides (I), (II), and (III) are readily dehydrofluorinated with formation of the corresponding olefins (IV), b.p. - 20°, (V), b.p. 17°, and (VI), b.p. 13°.

Found for I %: C 23,33; H 1,28; F 74,93; M 151
» » II %: C 23,88; H 1,06; F 74,76; M 202,8
» » III %: C 26,26; H 1,66; F 72,29; M 183
» » IV %: C 27,21; H 0,79; F 72,04; M 133
» » V %: C 25,98; H 0,67; F 73,13; M 182,6

On the basis of observations on the lowering of the rate of hydrogenation of the usual olefins [1] as we pass from ethylene, through propene, to isobutene, and also of Park's work [2] on the comparison of the heats of hydrogenation of $CH_2=CHCl$ and $CF_2=CFCl$, we may assume very confidently that the readiness with which hydrogenation occurs in the series of perfluoro olefins increases from tetrafluoroethylene to octafluoroisobutene. This is still being investigated.

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CURRENT EVENTS

ANNUAL GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE USSR

The Annual General Meeting of the Division of Chemical Sciences was held on March 24-25, 1958, in the auditorium of the Institute of Physical Chemistry of the Academy of Sciences of the USSR. The report of the most important achievements of the scientific establishments of the Division of Chemical Sciences of the Academy and its affiliated bodies during 1957 and on the science-organization activities of the Bureau of the Division was made by Academician N. N. Semenov, Academician-Secretary of the Division.

As a result of the achievements of our country during this notable year of the fortieth anniversary of the Great October Revolution, the legend of the weakness of Soviet science, spread so persistently by foreign propaganda, has crumbled away. All the peoples of the world have seen that , during the years of socialist development, the Soviet people have created a science that is in many respects in advance of the science of the U. S. and other technically advanced capitalist countries. Referring to the expression of thanks to the scientists, technologists and workers of the USSR made in the name of the Party and the government by N. S. Krushchev at the Jubilee Session of the Supreme Soviet, Academician N. N. Semenov said, "All this lays on us an exceptional responsibility: we must develop our science still more rapidly, be worthy of our great country, make new advances in science for the welfare of our fatherland, and we must not rest on our laurels, but pay special attention to the branches of science in which we lag behind, so that our position may be rectified and we may move to the forefront in all the decisive fields of science."

A considerable part of the report was devoted to an exposition of the most important achievements of the Institutes of the Division. Highly significant results were obtained in 1957 in the Institute of Physical Chemistry. Investigations on the adsorptional lowering of the strength and plasticity of metals made it possible to develop a theory of the action of active lubricants in the pressure treatment of metals and to devise some new active lubricants. The development of the theory of the formation of a double layer at a metal-semiconductor boundary has been completed. A potential theory of physical adsorption for adsorbents with an energetically heterogeneous surface has been created. As a result of the use of isotopes for the investigation of the mechanism of catalysis, new views on the mechanism of catalysis developed by the Institutes of Physical Chemistry and Chemical Physics have been confirmed. Progress has been made in investigations on electrochemical kinetics and in new investigations on the application of electrochemistry to the theory of structure. A theory has been developed on the passage of current across a semiconductor-electrolyte boundary. Interesting results have been obtained on the radiation-induced oxidation of organic compounds by the oxygen of an organic solvent. Weighable amounts of technetium have been isolated from molybdenum irradiated with neutrons, and some of its properties have been studied. Methods of breaking down thermal clouds and fogs, trapping silicosis-producing dusts, and protecting various objects from corrosion have been proposed for introduction into practice and are undergoing successful tests.

A shortcoming in the work of the Institute of Physical Chemistry is the poor coordination between the separate laboratories and sections.

In the year under review, further advances were made in the theory of chain reactions at the Institute of Chemical Physics. A theory was developed for the propagation of shock waves of small amplitude; it takes account of nonlinearity. The theory of thermal explosion, which originated at the Institute, was developed further and extended to the explosions of condensed explosive systems. A new method was developed for the oxidation of simple hydrocarbons in the liquid phase at temperatures and pressures close to the critical values.

Much progress has been made in the development of new apparatus. A new model of the "time magnifier"

has been designed for the study of very rapid processes; it enables one to work at 33 million frames per second. A new type of mass spectrometer has been devised. The principle on which it is based, the charge transfer of ions, makes it possible to obtain spectra containing comparatively few lines. Piezoelectric devices for the measurement of pressure have been devised. An electron paramagnetic resonance apparatus has been designed for the investigation of chemical kinetics. In the Anisotropic Structure Laboratory, new results on vitreous plastics have been obtained.

At the Institute of Macromolecular Compounds progress has been made in the production of thermostable polymers, including transparent polymers. New results have been obtained on the mechanism of catalytic polymerization. A new way of preparing block polymers varying in the number and size of blocks has been discovered. A relation has been established between the rates of breakdown and creep of polymers, and theories have been developed on the strength and deformability of oriented polymers and on intra- and inter-molecular action. Work on the stabilization of cellulose and its derivatives has been continued, and the mechanism of the oxidative degradation of cellulose ethers and esters has been elucidated. New products that have been developed include sorbents of high selectivity, scintillation plastics, and polyelectrolytes suitable for use in the improvement of soil structure, flotation, and coagulation. New apparatus has been devised for the study of the photoelastic effect and dynamic birefringence, for the study of reactions by the method of electron magnetic resonance, etc.

At the Institute of Heteroorganic Compounds new methods of synthesizing various heteroorganic compounds have been devised on the basis of theoretical views developed earlier. The alkylation of ferrocenes has been effected for the first time, and the orienting effects of various substituents have been determined. A new method has been found for the synthesis of tropylium derivatives. It was shown that there are great possibilities in the preparation of various heteroorganic compounds by the reaction of trialkylaluminum with the halides of various elements. Some interesting syntheses of sulfur-containing peptides have been carried out. Some new -ylide systems with charges shared with the aromatic ring have been synthesized. The development of the theory of tautomeric equilibrium has been continued.

A characteristic feature of the Institute of Heteroorganic Compounds is the effort made to apply the results of theoretical investigations to the solution of important practical problems, in particular the preparation of new monomers and polymers. Numerous investigations have reached the stage of application in industry: the synthesis of 7-aminoheptanoic acid for the manufacture of the fiber Enant, the synthesis of thiodivaleric acid, and the synthesis also of highly fluorinated compounds for plasticizers and lubricants.

Great interest is presented by materials of high thermal stability based on polyorganometallosiloxanes and rubberlike materials of high thermal stability based on organosilicon compounds. Many heteroorganic polymers containing phosphorus, silicon, germanium, tin, and other elements have been prepared. Work continues on the synthesis of new organophosphorus insecticides.

Investigations have been carried out at the Institute of Organic Chemistry over a wide front. New data have been obtained in confirmation of the structural and energetic principles of the multiplet theory. Progress is being made in investigations on the synthesis and properties of organoboron compounds of various types, organosilicon monomers, and vinyl compounds. A fundamentally new method of preparing macrocyclic compounds has been worked out on the basis of the opening of thiophene rings. Interesting results on the mechanisms of various reactions (azoxy coupling, isomerization of azoxy compounds) have been obtained by the use of labeled atoms.

Many of the investigations are of great importance for the national economy. A two-stage method has been worked out for the preparation of isoprene from isopentane in high yield. A rational multiproduct process has been developed for the treatment of petroleum residues: the preparation of gaseous olefins is combined with the simultaneous reduction of ores of nonferrous metals. New and effective methods of synthesizing various perfumes (nerol, geraniol, farnesol) have been developed and have been approved by the perfumery industry. New luminescent substances have been synthesized. It was shown that lignin oxidized with nitric acid can be applied successfully in the sinking of oil wells. An effective method has been found for the synthesis of the insecticide isodrine. It has been shown that valuable monohydric alcohols can be obtained in high yield by the hydrogenation of cheap pentosan-containing raw material in an acid medium.

In the Division of Petroleum and Gas Chemistry of the Petroleum Institute, work has been successfully completed on the synthesis of propene and polypropylene, the polymerization of ethylene to give high-melting

polyethylene, the study of the radiolysis of hydrocarbons by nuclear radiations, and the high-speed cracking of paraffins.

In the N. S. Kurnakov Institute of General and Inorganic Chemistry progress has been made in the investigation of the physicochemical properties of the compounds of rare elements: studies have been made of the effects of temperature, pressure, concentration, and other equilibrium factors on composition, structure, and reactivity. New results have been obtained on the chemistry of complex compounds. The development of a new theory on the hydration of ions in aqueous solutions has been completed. Industrial trials on a new method for the preparation of anhydrous stannous chloride and on a method for the refining of tin with the aid of chlorine have been carried out successfully. A new method has been developed for the group precipitation of platinum metals; it makes possible the almost complete extraction of all platinum metals from solutions in which they are present in very low concentration.

At the Institute of Silicate Chemistry a new method has been proposed for the preparation of chlorine-containing organosilicon compounds having a chain of alternating silicon and carbon atoms. It has been found possible to extend the range of application of the catalytic dehydrocondensation of trialkylsilanes with various organic hydroxy, oxo, and polyhydroxy compounds. It was shown that hexaalkyldisiloxanes can undergo cleavage under the action of alcohols, and this reaction provides a means of synthesizing organosilicon compounds. A series of investigations on the chief mineral of ceramics, mullite, and on the solid phases formed by heating oxides of elements of Group IV of Mendeleev's periodic system has been completed. The preparation of the monograph "Technology of the Grinding and Polishing of Glass" has been completed.

The Institute is making progress on the introduction into industry of special forms of protective coatings and impregnating preparations.

At the V. I. Vernadskii Institute of Geological and Analytical Chemistry progress has been made on the geochemistry of niobium, tantalum, zirconium, hafnium, molybdenum, the rare-earth elements, zinc, lead, uranium, and boron. Investigations have continued on the determination of the absolute geological age of rocks by radioactivity methods. New biogeochemical provinces have been discovered. With the aid of neutron core-sampling a rich boron deposit has been discovered. In analytical chemistry methods have been developed for the determination of many chemical elements with the aid of spectra, x-ray spectra, and oscillographic, chromatographic, and radioactivity procedures. Investigations on nuclear chemistry have continued satisfactorily.

At the V. G. Khlopin Radium Institute, experimental confirmation has been found of the previously discovered cis effect in the complex compounds of bivalent platinum. Progress has continued in the investigation of the properties of various compounds of uranium, thorium, plutonium, radiozirconium, radioniobium, and the rare earths. Interesting results have been obtained in the investigation of the behavior of substances in solutions at extreme dilutions. Progress has been made in the investigation of the mechanism of the fission of complex nuclei under the bombardment with fast particles, in the study of the nature of cosmic rays, and in the determination of absolute geological age. A method has been developed for the preparation of photographic emulsions of particularly fine grain and high sensitivity.

At the Hydrochemical Institute progress has continued in the investigation of the physicochemical conditions for the formation of natural waters and the changes in the hydrochemical regime of reservoirs resulting from hydrotechnical construction.

At the Kazan Affiliated Institute of the Academy new organophosphorus and organoarsenic compounds have been synthesized and investigated. A new method has been developed for the synthesis of phosphoramidic esters substituted in all sorts of ways. A procedure has been proposed for the synthesis of the free radical 2,2-diphenyl--1-picrylhydrazyl. Extensive tests are being carried out on the insecticides Octometine and Dithiophos and on the medicinal preparation Phosorbine. Investigations are continuing on the oil and natural gases of deposits in the Tatar Republic.

At the Urals Affiliated Institute of the Academy a rational method has been worked out for the treatment of dusts and sublimates so as to extract the rare elements. Investigations have been carried out on the electrolysis of rare metals and in a search for a solid electrolyte for the fuel element. A quantitative characterization has been made of the reactivity of the benzene nucleus in alkylation by olefins as affected by the nature of the catalyst, the identity of the alkyl groups, and the temperature of the process. Results of practical importance have been obtained on the production of high-grade jet-engine and diesel fuels.

At the Bashkir Affiliated Institute investigations are proceeding successfully on new methods of treating sulfur-containing petroleums.

In summarizing, the speaker pointed out that in recent years, and particularly in 1957, there had been great achievements in organic synthesis and in the theory of the structure and reactivity of organic substances. For this we are indebted, above all, to the Institute of Heteroorganic Compounds, which is rapidly becoming one of the most important centers for the chemistry of heteroorganic compounds in the world. Substantial progress is being made in petrochemistry and heavy organic synthesis, though the rate of progress in this field cannot be regarded as adequate. We must intensify our investigations in polymer chemistry and on the synthesis of natural and biologically important compounds. In inorganic chemistry, work is proceeding at a satisfactory level on the chemistry of complex compounds, particularly of the platinum metals, and on radio- and geo-chemistry. Some progress has been made in the chemistry of rare elements, but it is here necessary to move forward on a much broader front. Inadequate investigation has been devoted to general questions of inorganic chemistry, valence theory, thermochemistry, and the chemistry of semiconductors.

In physical chemistry work is proceeding at a satisfactory level at the Institutes of the Division in the fields of surface phenomena, chemistry of electrode processes, chemical kinetics and catalysis, and combustion and explosion. Quantum mechanics is still not applied sufficiently in chemistry. Our backwardness in the establishment of the use of modern physical and physicochemical methods of investigation is mainly due to the lack of the necessary instrument-making organization.

* * *

The second part of the report was devoted to activities concerned with the organization of scientific work. In the year under review attention has been devoted mainly to discovering and intensifying the most promising lines of work, to setting up the necessary organization to sustain new directions in science, and to the concentration of efforts on the solution of the most important problems. In the solution of important problems, the Bureau has used extensive cooperation of workers of the Institutes of the Division, of branch institutes, of the State Planning Commission, of the State Scientific and Technical Commission, of the Ministry of Chemical Industry, of the universities and of the Councils of the National Economy. Much attention was devoted to the organization of scientific investigations during the Seven-year Plan.

The following are regarded as the most important problems for solution in 1959-1965: 1. The scientific principles underlying the preparation of macromolecular compounds, monomers, and auxiliary products. 2. The chemistry of natural and biologically important compounds. 3. The chemistry of semiconductors and electrochemical sources of current. 4. The chemistry of rare elements. 5. Radioisotopes and radiations in chemistry. 6. Synthesis of heteroorganic compounds and their utilization in the national economy. In collaboration with other Divisions of the Academy of Sciences problems on geochemistry and the interaction of high-energy particles with matter will be resolved.

It is proposed that, of the efforts and resources of the Institutes of the Division, the affiliated bodies, and the republic academies, about 50% will be spent in the solution of the most important problems, about 30% will be spent in the solution of theoretical problems and on exploratory investigations, and about 20% on the solution of other important problems. For each of the most important problems extensive programs of investigations covering the next seven years will be composed and discussed, and the action required to support these programs will be planned. Special attention has been given to the development of the chemistry of macromolecular compounds. Much work has been done on the question of liquidating our backwardness in the manufacture and application of polymers and of widening our research in this field. The Division, with the Ministry of Chemical Industry and the Ministry of Higher Education, has participated in the work of the State Planning Commission on the preparation of a draft government order envisaging a very considerable development of investigations on polymers. The problem of polymers is the main problem of the Division. In order to direct all the scientific investigations carried out in association with the Division, a Polymer Council has been set up; it is made up of leading workers from the Academy, branch institutes, and industry, and also of representatives of the State Planning Commission, the Ministry of Chemical Industry, and the State Scientific and Technical Commission. Scientific investigations on polymers will be extended considerably in most of the institutes of the Division; they will be carried out in close coordination with other scientific establishments.

Much attention was devoted to the development of chemistry in the Siberian Division. It is planned to establish a network of chemical institutes in Siberia in the near future. Prominent scientists have been recommended as directors of the work of these institutes. Teams of young enterprising scientific workers, who are very willing to move to Siberia, are being trained. There have been discussions on the most important of the topics with which the new institutes will occupy themselves. Academician N. N. Semenov stated, "the Chemical Group of the Siberian Division, both with respect to the high qualifications of its directors and as a complex of institutes, will be sufficiently strong and versatile in 4-5 years time to compete successfully with Moscow."

There has been some success in the year under review in the introduction of the most important achievements of science into the national economy, but the results of investigations are generally introduced too slowly with enormous waste of time and effort by scientific workers. The Bureau of the Division is taking steps to solve problems of organization, but it is impossible to deal with this matter on our own. It is essential to solve the question of the assimilation of the achievements of science at a higher and broader national level. In this matter it is of great importance to establish a closer association with local organizations, particularly with the Councils of National Economy. This would probably be helped by some decentralization of the direction of scientific establishments of the Academy of Sciences, e.g. by the setting up of affiliated bodies of the Division in the large centers (Leningrad, Kazan').

In reviewing the conferences and symposia held in accordance with the plan of the Division in 1957, we must regard their results as on the whole satisfactory. The main defect, obstinately retained by the leaders, of the organizing committees, was the unwieldiness of the papers and the consequent inadequate time for discussion. More careful watch must be kept on the realization and implementation of proposals and recommendations made at conferences.

The year under review was characterized by the establishment of closer relations with foreign scientists, particularly those from the people's democracies. Agreements on scientific cooperation have been concluded with scientific organizations of several countries. More than 180 scientists went abroad, and more than 200 foreign scientists visited Institutes of the Division. About 150 papers and communications were presented by scientists of the Division at international conferences and congresses. Much work has been done to strengthen international relations and increase their effectiveness. In the first place we contemplate participation in those international undertakings that are of great significance for the development of the most important branches of chemistry.

As before, the large accumulation of material at the editorial stage in all journals of the Division creates a bottleneck in the Division's work. The time between the receipt of a paper by the editor and its publication has increased to an extent which cannot be tolerated. The Bureau of the Division is at present taking steps to correct the position that has arisen.

The following took part in the discussion of the report: Academicians A. E. Arbuzov, A. P. Vinogradov, S. I. Vol'fkovich, I. L. Knuniants, A. N. Frumkin, Corr. Members of the Academy S. N. Danilov, B. V. Deriagin, I. A. Kazarnovskii, I. E. Starik, Doctors of Science V. T. Bykov, K.M. Gorbunova, V. I. Ivanov, N. A. Toropov, and others.

An active discussion centered on the question of the establishment of affiliated bodies of the Division. In the speeches much attention was given to the organization of investigations on the most important topics, particularly polymers and the assimilation of the achievements of science in the national economy. Academician A. E. Arbuzov, in some very pointed remarks, raised the question of the necessity of taking immediate radical measures to improve the provision of reagents and modern scientific equipment. Academician I. L. Knuniants pointed out that the Bureau of the Division was concerned with important questions of Soviet chemistry. The part to be played by the Bureau of the Division in the general national task of developing work on the chemistry of polymers was emphasized also by the Academician-Secretary of the Division, Academician N. N. Semenov.

The General Meeting approved the activities of the Bureau of the Division of Chemical Sciences as a whole and took note of the main tasks to be undertaken in the next period.

ALL-UNION CONFERENCE ON CHROMATOGRAPHY

A conference on chromatography called by the Chromatography Commission of the Division of Chemical Sciences of the Academy of Sciences of the USSR was held on February 3-6, 1958. The conference was concerned with the theory and application of ion-exchange and adsorption chromatography and also the possibility of applying different kinds of chromatography in the analysis and separation of substances. The work of the conference was carried out at plenary sessions and in three sections. In all, about sixty papers were read.

In opening the conference, the chairman of the Chromatograph Commission pointed out the great importance of chromatography in modern science. In recent years the methods of chromatography have developed rapidly and show great promise of further development. Considerable progress has been made in the theory of nonequilibrium chromatography and new methods of chromatothermography. Some new resins have been synthesized, the technology of the manufacture of ionites has been improved, and various new and automatic apparatus and arrangements have been developed for chromatographic purposes. The quality of chromatographic paper has been improved. In the field of industrial chromatography investigations and trials have been carried out on demineralization plants under the conditions of use in thermal power stations working at superhigh and supercritical steam parameters. Laboratory methods have been proposed for the preparation of ionite membranes.

In the papers on the theory of chromatography it was noted that the theory of nonequilibrium chromatography has been developed in the investigations of S. E. Bresler, A. A. Zhukhovitskii, O. M. Todes, and N. N. Tunitskii. A. A. Zhukovitskii and O. M. Todes developed the theory of the frontal process, and N. N. Tunitskii worked out the theory of nonequilibrium chromatography on the basis of statistical methods. S. E. Bresler proposed a general differential equation for nonequilibrium chromatography; it was a material-balance equation. Bresler succeeded in taking account of the delay in establishing equilibrium as a result of the diffusion of the adsorbate in the grains of adsorbent and in the spaces between the grains. His proposed equation is applicable to elution, frontal, and displacement chromatography and to ion exchange.

A. A. Zhukhovitskii and N. M. Turkel'taub examined the conditions determining the applicability of chromathermography and of the thermodynamic method for the complete separation of the components of a mixture; they designed new chromatographic apparatus for the analysis of gases, and also chromatographs and chromthermographs based on partition and development chromatography with continuous passage of the mixtures to be analyzed; they gave the theoretical basis of the operation of this apparatus. The analysis of gas mixtures by such methods is of great current importance, but unfortunately its introduction into industry has been unjustifiably delayed. Moreover, the necessary standard sorbents have not been made available.

O. M. Todes drew attention to the evolution of heat in the chromatography of gases with resulting effects on the dynamics of adsorption and desorption. M. M. Seniavin examined the possibility of predicting optimum conditions for the separation of mixtures by ion exchange, and he studied the conditions required for the separation of some mixtures of rare elements for analytical and preparative purposes. F. M. Shemiakin pointed out that the distribution of the substances to be separated between two immiscible phases is characteristic of chromatography as a whole, and he proposed a general formulation for the process of chromatographic separation. It has become necessary to unify the terminology of chromatographic concepts and processes and to adopt uniform notations, and for this purpose we must work out concrete formulations of concepts and processes. Nonsorbing carriers do not exist, and different chromatographic mechanisms often proceed simultaneously. G. M. Samsonov studied and formulated the laws of the statics and dynamics of the sorption of complex ions. V. V. Rachinskii proposed a theory for the dynamics of ion exchange between ions of different valences, and it was confirmed by experiments of the author and N. N. Tunitskii. K. M. Saldadze studied the effect of the structure of the cationite on processes of cation exchange on KU resins of various brands, prepared both by condensation and by polymerization; he studied the exchange of ions on anionites differing in basic character: AN-9, AN-2F, EDE-10P, and AV-16. N. N. Tunitskii and E. P. Cherneva proposed a theory of the separation of rare-earth elements by chromatography; they studied the kinetics of ion exchange on cationites in the form of grains and membranes and the effect of the concentration of sulfo groups in unifunctional strongly acid cationites on equilibrium selectivity. N. M. Turkel'taub examined the most important physicochemical parameters of partition chromatography. A. T. Khalezova and K. A. Gol'bert studied the kinetics of the adsorption of vapors by activated charcoals. S. Iu. Elovich studied the possibility of applying chromatography for the separation of complex compounds on the resin KU-2.

A. B. Pashkov examined the preparation of modern ionites based on copolymers of styrene and divinylbenzene, and also methods of granular copolymerization. He has worked out methods of sulfonation, nitration, and chloromethylation of copolymers, and the introduction of amino and phosphoric acid groups. N. G. Polianskii studied the thermal stability of KU-1 and KU-2. V. S. Titov described various methods of preparing ionite membranes and studied their properties. Ionite membranes have high electrochemical activity; they show selective permeability to cations and anions. Membranes having strongly acid, weakly acid, strongly basic and weakly basic groups were prepared. For the preparation of membranes, finely divided ionites were cemented together with highly polymeric substances. The membranes can be applied in the demineralization of water. The electrode properties of membranes were studied by E. A. Materova with a view to their utilization as hydrogen and sodium electrodes.

I. P. Alimarin, Corr. Member Acad. Sci., and T. A. Beliavskaia carried out the separation of titanium and zirconium from accompanying elements by the ion-exchange method. A. P. Kreshkov and E. N. Saiushkina studied the conditions for the separation of the cations of three analytical groups by the same method. T. B. Gapon and A. M. Gurvich proposed a method for the separation of metals by the formation of adsorption complexes. S. M. Chernobrov proposed to separate niobium from tantalum and titanium on the anionite EDE-10P. K. M. Ol'shanova developed a method of chromatographic qualitative analysis of cations and anions in alumina columns and proposed a new classification of cations and anions on this basis. K. M. Ol'shanova and co-workers developed methods of precipitation and oxidation-reduction chromatography on alumina, glass powder, and quartz sand.

F. G. Prokhorov reported on his investigation and industrial trials of apparatus for the complete chemical demineralization of water, and he examined the factors affecting the extent of demineralization and also various schemes of demineralization in the production of steam having superhigh and supercritical parameters in thermal power stations. P. A. Avramenko gave an account of his experience in the working of demineralization plants under the conditions applying at power stations. O. S. Lenchevskii studied electrochemical methods of demineralizing water.

Several papers provided illustration of the fruitful application of chromatography in biochemistry, medicine and pharmacy. A. G. Vereshchagin studied the separation of the higher fatty acids in plant tissues by the method of inverted-phase partition chromatography. A. E. Gurvich studied protein antigens and antibodies by paper chromatography. A. S. Spirin proposed a method of quantitative paper chromatography for the analysis of nucleotides and the nitrogenous bases of the nucleic acids of bacteria. Iu. A. Pankov separated, identified, and quantitatively determined corticosteroids. F. M. Shemiakin and E. S. Mitselovskii proposed a new method of paper electrochromatography of medicinals. F. M. Shemiakin, V. N. Bogdanova, and O. S. Lobakhina examined the possibility of analyzing liquids of the organism chromatographically with detection of various sulfanilamide preparations. E. V. Shtannikov studied the possibility of utilizing ion-exchange resins in medicine. Apart from these, many other papers were presented, but owing to lack of space we cannot discuss them here.

At the plenary session a paper was read by the Polish scientist W. Kemul on a new chromatopolarographic method of analysis which is applicable both to inorganic and to organic substances. The method is very promising and can be carried out both with columns of sorbents and on strips of paper.

The discussion on the papers revealed the existence of various controversial questions on the theory of chromatography and in the preparation and application of sorbents. With regard to the theory of chromatography there are many contradictory views and opinions, which received lively discussion, but were not altogether resolved. The discussion of these questions will be continued in the scientific journals. The conference recommended that investigations in the theory of chromatography should be developed further, particularly with a view to the prediction of optimum conditions for the separation of complex mixtures, and that calculating machines should be used in the solution of the differential equations concerned. It is necessary to develop the application of partition chromatography and the theory and practice of the application of organic reagents and solvents in chromatography. It is necessary to perfect the technology of manufacturing chromatographic alumina and silica gel, to draw up a plan for the organization of the industrial production of ionites and ionite membranes, and to market particularly pure sorbents for the medicinal and food industries. The conference recommended that the biological activity of ionites and their harmlessness for organisms should be investigated.

The All-Union Conference was highly successful and revealed that there had been a great expansion in investigations on chromatography in the Soviet Union in the four years that had elapsed since the 1953 conference.

However, there were very few papers on partition chromatography, though it is this branch that has made most headway in other countries. There were no papers on luminescent chromatography. The precipitation chromatography proposed by E. N. Gapon has not yet received adequate development.

F. M. Shemiakin

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

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